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Synthesis and the optical and electrochemical properties of indium(III) bis(arylimino)acenaphthene complexes

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ABSTRACT: Aryl bis(imino)acenaphthenes (Ar-BIANs) are well-established rigid and sterically bulky diimine ligands, which are redox non-innocent and versatile π-acceptors due to their low-lying π* orbitals, and are frequently used to bind transition metals. However, the coordination chemistry of Ar-BIAN ligands to main group elements is not as well developed as their transition metal counterparts. In particular, there are no comprehensive studies describing the spectroscopic and electrochemical properties of main group Ar-BIAN complexes. Herein, we report the synthesis and full characterization of a series of new indium(III) Ar-BIAN complexes, bearing 2,6-dialkyl (**1b** and **2b**), 4-nitro (**3b**), and 4-dimethylamino (**4b**) groups at the aryl-diimine part of the ligand. Their optical and electrochemical properties have been revealed by

UV-vis spectroscopy and cyclic voltammetry, respectively. Additionally, DFT calculations were performed to gain insights into the nature of the properties displayed.

INTRODUCTION

Redox processes and redox-active ligands play important roles in modern chemical transformations constituting exciting areas of research in coordination and organometallic chemistry,[1] and catalysis.[2] The term "*innocent ligand*" was first coined by Jørgensen as a ligand that allows the oxidation states of the central atoms to be readily determined.[3] In contrast, "*non-innocent ligands*" refer to ligands in metal complexes where the oxidation states are ambiguous and need to be experimentally determined.[1] Non-innocent ligands have energetically accessible electronic levels rendering these species redox active at mild potentials.[4] Aryl bis(imino)acenaphthenes (Ar-BIAN) belong to one class of non-innocent ligands. Ar-BIAN ligands were first reported in the 1960s and have been widely investigated as robust ligands for catalytically active transition metal centers since the early 1990s.[5] Although many coordination complexes between transition metal and Ar-BIAN ligands have been described,[6-10] their main group and lanthanide counterparts remain poorly explored, with a limited selection of main group Ar-BIAN complexes being synthesized and crystallographically characterized.[11-12]

Ar-BIAN ligands are highly tunable species that are readily synthesized from cheap and commercially available anilines and acenaphthenequinone.[13-14] Functionalized Ar-BIAN compounds are acknowledged as oxidatively and thermally stable ligands for transition metal centers. The extensive π-system of the acenaphthene ring combined with the sterically modular aniline provide a broad range of π-acceptor frameworks, offering precise control over the steric, optical, and electronic properties.[14-15] Consequently, Ar-BIAN ligands have been employed in the preparation of numerous transition metal molecular compounds, which could be of use in photosensitization applications due to the characterized MLCT (metal-to-ligand charge transfer) transition from the d-orbitals of the transition metal to the π* orbitals of the Ar-BIAN ligand.[9-10, 16] The low-lying π* orbitals of Ar-BIAN ligands have been successfully exploited as 'capacitors' for multi-electron reductions in redox non-innocent ligands.[17-19] Consequently, there have been reports of transition metal Ar-BIAN complexes being used as catalysts for organic reactions such as cycloaddition of azides and alkynes,[7-8] as well as olefin polymerization, work that had been pioneered by M. Brookhart and coworkers using Ni(II) and Pd(II) Ar-BIAN complexes.[20-27] More recently, Cu(II) Ar-BIAN complexes have been investigated as catalysts for the reverse atom transfer radical polymerization (ATRP) of styrene.[28] Moreover, applications of Cu(I) Ar-BIAN complexes as light harvesters that can absorb to the NIR region have also been reported.[6, 9, 16]

In terms of main group chemistry, however, groups 1 and 2 constitute majority of the Ar-BIAN main group metal complexes.[17-19, 29-35] In these examples, each Ar-BIAN ligand undergoes facile reduction due to its electron accepting nature to form the corresponding metal complex.[11] With respect to Group 14 metals, a small number of complexes have been previously reported. For instance, *N*-heterocyclic germylenes that contain anionic Ar-BIAN ligands include [(dipp-BIAN)Ge:], [(dtb-BIAN)Ge:] (dipp = 2,6-diisopropylphenyl, dtb = 2,5-(*t*-Bu)$_2$Ph), and [(bph-BIAN)Ge:] (bph = (2-PhC$_6$H$_4$)).[36] Moreover, complexes such as (dipp-BIAN)GeCl have been prepared by reacting the neutral Ar-BIAN ligands with GeCl$_2$, where the GeCl$_2$ acts as a reducing agent for the Ar-BIAN ligands to form their radical anionic counterparts.[37-38] On going down this group, tin complexes supported by neutral Ar-BIAN ligands have also been described, including [(mes-BIAN)SnCl$_4$] (mes = 2,4,6-trimethylphenyl) and [(dtb-BIAN)SnCl$_2$]).[12, 38-39] A series of group 15 and 16 Ar-BIAN metal complexes have been previously characterized as well. For example, [(dipp-BIAN)$SbCl_3$ and [(mes-BIAN)$BiCl_3$])[12] supported by neutral Ar-BIAN ligands, and [(dipp-BIAN)E] [$SnCl_5$•THF] obtained by reduction of ECl_3 (E = P and As) with $SnCl_2$, followed by treatment with dipp-BIAN to give their dianionic form.[40] As for the chalcogens, the reaction of TeI_4 with neutral dipp-BIAN results in a two-electron reduction of the metal center to form [(dipp-BIAN)TeI_2], in which the ligand is neutral and the chalcogen has been reduced to the +2 oxidation state.[41] More recently, the (dipp-BIAN)$SeCl_2$ and (dipp-BIAN)$SeBr_2$ counterparts have also been described.[42] Clearly, the redox non-innocence of Ar-BIAN ligands have contributed to some rich chemistry and oxidation state ambiguity even among main group coordination compounds.

In the case of group 13 complexes, other than a limited number of boron compounds,[39, 43] only a few aluminum and gallium Ar-BIAN complexes have been isolated and structurally characterized.[43-49] In particular, until very recently,[50] there was only one crystallographically characterized example of a monometallic Ar-BIAN indium(III) complex,[12] and two reports presenting the related tetrakis(imino)py-racene (TIP) ligand.[51] Hence, the synthesis of new, heavy group 13 Ar-BIAN complexes and the evaluation of their absorption and electrochemical properties still remain under-explored areas.

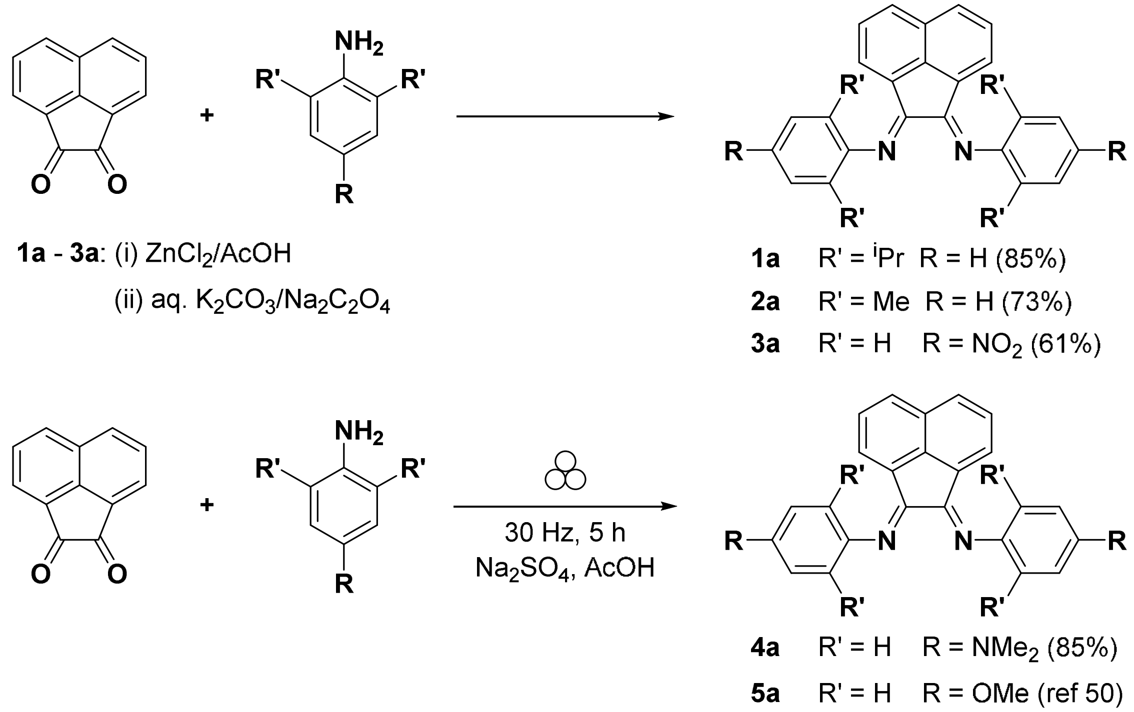
Our group is interested in applying mechanochemical approach to synthetic main group compounds[52] and has recently reported the preparation of new indium(III) bis(arylimino)-acenaphthene complexes by using an essentially solvent-free mechanochemical approach.[50] The indium(III) complexes were characterized by density functional theory (DFT) calculations, electrochemistry, and UV-Vis-NIR spectroscopy. The electrochemical data suggested that the Ar-BIAN indium(III) complexes could be converted to their indium(I) congeners by mild reducing agents, offering us the opportunity to explore the intriguing redox non-innocence of the Ar-BIAN systems. Upon reduction of the indium(III) center, these complexes show potential for applications as photosensitizers, dovetailing with our interest in the use of Earth-abundant elements in artificial photosynthesis.[16, 53-55]

Herein, we present a family of new indium(III) Ar-BIAN complexes with the synthesis of a broad range of Ar-BIAN ligands comprising electron-donating and electron-deficient substituents on the arylimino fragment. All of the complexes reported here have been structurally characterized, and probed with electrochemical and UV-vis spectroscopic measurements, as well as DFT and TD-DFT calculations.

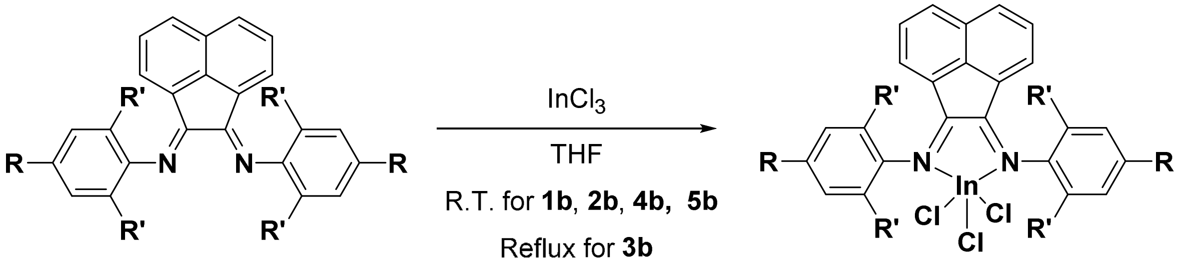
RESULTS AND DISCUSSION

Synthesis of complexes

The alkyl- and nitro-substituted Ar-BIAN ligands (**1a**-**3a**) were synthesized by condensation of acenaphthoquinone with the corresponding aniline under acidic conditions.[56-57] The Lewis acidic $ZnCl_2$ was used as the templating agent, after which de−metalation with K_2CO_3 or $Na_2C_2O_4$ was carried out (Scheme 1, top half). However, this method proved unsuccessful for the synthesis of the *para*-amino-substituted **4a**, and ligand hydrolysis was observed after the de-metalation step in an aqueous $Na_2C_2O_4$ solution. Alternatively, we have previously demonstrated that substituted Ar-BIAN ligands can be successfully synthesized *via* mechanochemical methodologies, which bypass the $ZnCl_2$ templating and subsequent de-metalation step.[50] Accordingly, **4a** was prepared via a ball-milling mechanochemical approach in the presence of a catalytic amount of acetic acid and Na_2SO_4 (Scheme 1, bottom half). The synthesis of **5a**, which we previously reported, has been included in Scheme 1 for the completeness of our study.[50] In a typical procedure, all reactants and additives were loaded into a stainless steel grinder jar containing a 10 mm stainless steel ball (4 g weight). The reaction mixture was milled for 5 h in a Retsch MM400 mixer mill operating at 30 Hz.[58, 59] Based on the ^{1}H NMR spectra, **4a** was formed with only trace amounts of unreacted precursors. Subsequent reaction of the Ar-BIAN ligand (**1a** – **5a**) with $InCl_3$ in tetrahydrofuran (THF) afforded the respective indium(III) Ar-BIAN complexes (**1b** – **5b**). The syntheses of **1b**, **2b**, **4b**, and 5**b**[60] were conducted at room temperature, whereas **3b** was prepared under reflux conditions in THF (Scheme 2).



Scheme 1 General synthetic scheme of Ar-BIAN ligands **1a** – **5a**. The symbol for mechanical milling above the arrow of the equation in the lower half has been proposed by Hanusa *et al.*[58]



1a	R' = ^{i}Pr	R = H
2a	R' = Me	R = H
3a	R' = H	R = NO_2
4a	R' = H	R = NMe_2
5a	R' = H	R = OMe

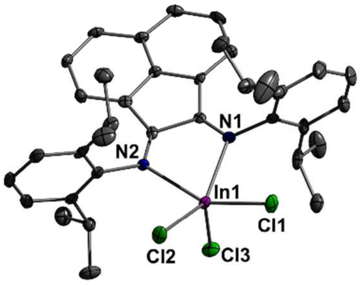
1b	R' = ^{i}Pr	R = H (76%)
2b	R' = Me	R = H (41%)
3b	R' = H	R = NO_2 (64%)
4b	R' = H	R = NMe_2 (68%)
5b	R' = H	R = OMe (ref 50)

Scheme 2 Synthetic route to **1b** – **5b**.

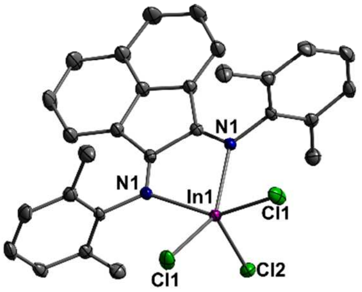
Spectroscopic and Crystallographic Studies

The ^{1}H and ^{13}C{^{1}H} NMR spectra obtained for **1b** to **5b** concurred with the formation of coordinated, neutral Ar-BIAN ligands on indium(III). In general, the ^{1}H NMR spectra of the coordinated Ar-BIAN ligands in complexes **1b** to **5b** each exhibit a downfield shift compared to the corresponding spectra of the ligands **1a** to **5a**. Compounds **1b** and **2b** were purified by recrystallization from 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF), respectively. In the case of **3b**, single crystals suitable for single crystal X-ray diffraction analysis were obtained by recrystallization from acetonitrile (ACN); however, batch purification was carried out by slow diffusion of diethyl ether (Et_2O) into DMF. Therefore, the characteristic DMF signals were present in the ^{1}H NMR spectrum of **3b** recorded in deuterated acetone (SI, Fig. S5). In the case of **4b** and **5b**, vapor diffusion of Et_2O into DMF has been used for recrystallization and, hence, one DMF molecule is coordinated to each indium(III) metal center. Thus the ^{1}H NMR spectra for both complexes reveal signals corresponding to DMF (SI, Fig. S6 and S8). All indium(III) Ar-BIAN complexes were successfully recrystallized to provide samples suitable for single crystal X-ray structural analyses (Fig. 1). We have already previously reported two structures, [(*p*-

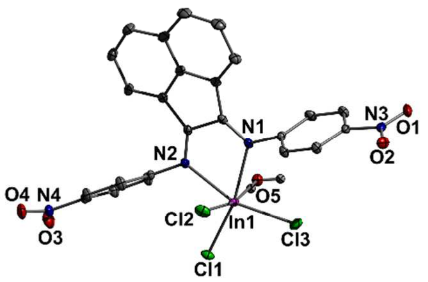
MeOAr-BIAN)$_2$InCl$_2$]$^+$[InCl$_4$]$^-$ (**6**) and (*p*-BrAr-BIAN)InCl$_3$ (**7**), which we compare with and refer to in this report for the completeness of our studies.[50] Compound [(*p*-MeOAr-BIAN)$_2$InCl$_2$]$^+$[InCl$_4$]$^-$ (**6**) was originally recrystallized from ACN; however, when **6** is recrystallized from a more strongly coordinating solvent like DMF, the mono Ar-BIAN complex **5b** is formed. We attribute the formation of **5b** to the stronger coordinating ability of DMF compared to ACN. Coordinating solvents (H_2O in **3b**, DMF in **4b** and **5b**) are bound to each indium center resulting in distorted octahedral geometries for the complexes. The equatorial bond angles range from 72.64(5)° to 101.06(2)° in **3b**, 72.85(10)° to 97.94(8)° in **4b**, and 72.68(5)° to 96.77(4)° in **5b**, deviating significantly from the ideal value of 90°. Similarly, the axial bond angles (166.45(4)°, 164.01(7)°, and 162.18(4)° in **3b** to **5b**, respectively) also deviate from the expected 180°. This deviation of axial and equatorial bond angles in a distorted octahedral geometry was also reported in a similar mes-BIAN-InCl$_3$ complex.[12] In contrast, **1b** and **2b** adopt distorted square pyramidal geometries presumably due to the increased steric hindrance around the metal nucleus introduced by substitution of isopropyl (in **1b**) and methyl (in **2b**) groups at the *ortho* positions of the aniline moiety. The axial bond angles range from 95.89(13)° to 110.12(6)° in **1b** and from 100.86(4)° to 107.42(19)° in **2b**, which are similar to those in the related tetrakis(imino)pyracene (TIP) complexes that also adopt distorted square pyramidal geometries around the indium center (94.2° – 117.4°).[51] Complex **2b** exhibits a plane of symmetry bisecting the acenaphthene fragment and the indium metal center, making the two diimine N and Cl atoms at the equatorial positions equivalent. The C-C and C-N bond distances within the diimine moiety in **1b** – **5b** (ranging from 1.517(3) Å to 1.535(8) Å and from 1.274(2) Å to 1.288(4) Å, respectively) are consistent with typical of C-C and C=N bond lengths.[12] Therefore, complexes **1b** – **5b** can be considered to consist of neutral Ar-BIAN ligands coordinated to indium(III) *via* dative bonds. The average In-N bond distances for **1b** and **2b** (2.341 Å and 2.320 Å, respectively) are slightly shorter than their mes-BIAN-$InCl_3$[12] and the dipp-TIP-$InCl_3$ counterparts (2.35 Å and 2.38 Å).[51] The introduction of an electron withdrawing -NO_2 group (in **3b**) and electron donating -NMe_2 (in **4b**) and -OMe groups (in **5b**) did not affect the average In-N bond distances greatly. Their average In-N bond distances (2.317 Å in **3b**, 2.324 Å in **4b**, and 2.331 Å in **5b**) remained similar to that for **1b** and **2b**. Notably, complexes **1b** to **5b** all exhibit In-Cl bond distances significantly longer than that for $InCl_3(THF)_2$ (2.331(3) Å).[61] The In-Cl bond distances in **1b** and **2b** range from 2.3643(17) to 2.3897(5) Å and are shorter than those in the related mes-BIAN-$InCl_3$, likely due to the increased electron donation from the mes-BIAN ligand in the latter, resulting in a weakening of the In-Cl bonds.[12] Although **4b** and **5b** bear ligands that are more electron-rich than **3b**, the average In-Cl bond distances in these complexes are similar (2.425 Å, 2.423 Å and 2.426 Å in **3b**, **4b**, and **5b** respectively).



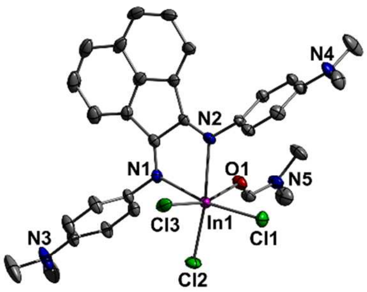
1b



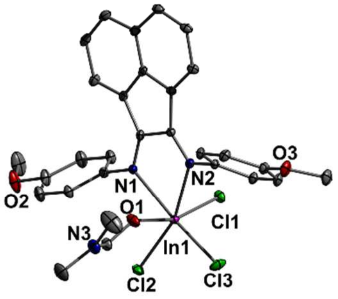
2b



3b



4b



5b

Figure 1. Selected bond lengths (Å) and angles (°) of complexes (**1b**) In1-N1 2.342(5), In1-N2 2.339(5), In1-Cl1 2.3835(16), In1-Cl2 2.3800(17), In1-Cl3 2.3643(17); (**2b**) In1-N1 2.3196(15), In1-Cl1 2.3897(5), In1-Cl2 2.3769(7); (**3b**) In1-N1 2.3230(14), In1-N2 2.3114(14), In1-Cl1 2.4013(4), In1-Cl2 2.4722(5), In1-Cl3 2.4032(5), In1-O5 2.2733(13); (**4b**) In1-N1 2.317(3), In1-N2 2.331(3), In1-Cl1 2.4029(10), In1-Cl2 2.4241(9), In1-Cl3 2.4408(10), In1-O1 2.259(3); (**5b**) In1-N1 2.3182(14), In1-N2 2.3444(13), In1-Cl1 2.4417(4), In1-Cl2 2.4301(4), In1-Cl3 2.4058(5), In1-O1 2.2306(13). Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Absorption and electrochemical studies

To understand the absorption profile of the indium(III) complexes, UV-vis absorption spectroscopic measurements were carried out for **1b** – **5b**. The absorption spectra obtained for each of the complexes at 298 K are depicted in Fig. 2. Complexes **1b** to **5b** typically exhibit two major sets of absorption bands. The bands are assigned to a mixture of the intraligand π-π* charge transfer transitions between the arylimine and the acenaphthene motifs, according to the TD-DFT calculations (*vide infra*). The spectrum is significantly red-shifted when the electron donating –NMe$_2$ group is present on the di(arylimino) moiety, inducing a smaller HOMO-LUMO gap due to a more destabilized HOMO. Although inductively electron-rich alkyl groups are present in **1b** and **2b** (*i.e.*, 2,6-diisopropyl and 2,6-dimethyl), the effect is not as strong as the mesomerically donating groups in **4b** and **5b** (*i.e.*, 4-dimethylamino and 4-methoxy). This is consistent with DFT theoretical calculations from the Zysman-Colman group, where they reported that the HOMO of the ligand is destabilized by 1.1 eV when a mesomerically electron donating (-NMe$_2$) group is present within the ligand backbone, whereas a destabilization of only 0.29 eV is achieved when an inductively electron rich alkyl (2,4,6-trimethyl) group is introduced.[14] The single intense absorption band at *ca.* 320 nm in **3b** may result from a coincidental convergence of multiple intraligand charge transfer transitions.

With an initial objective to identify a suitable reducing agent with an adequate reduction potential to obtain the indium(I) counterparts of complexes **1b** to **4b**, their redox properties were examined by cyclic voltammetry. The redox potentials of accessible reduction and oxidation waves are summarized in Table 1. The voltamogram for **5b** has not been collected in this report since its redox potential is expected to be identical to the previously reported compound **6**, which has been recorded in ACN. Since the molecular structures of **5b** and **6** are solvent dependent, their redox potentials would be affected by the solvent used.[50] All potentials are reported relative to the ferrocenium/ferrocene (Fc^+/Fc) redox couple. A direct comparison of the voltamograms of **1b** to **4b** cannot be made due to their disparate solubility properties and the differences in their coordination spheres. However, it is worth noting that the electrochemical behavior of **1b**, **2b**, and **3b** consist of four irreversible reductions and a series of oxidations (Fig. 3). The irreversibility may stem from the following. Firstly, detachment of a chloride ligand or coordination of a solvent molecule to the indium species formed during the voltammetric sweep may occur, since the reduction of the indium(III) center may involve structural changes arising from the anion dissociation. Secondly, the ligand itself may reduce due to its non-innocent nature. Thirdly, the putative indium(I) intermediates formed at the electrode surface may disproportionate, which is also supported by the experimental findings (*vide infra*). In contrast, the electrochemical behavior of **4b** in DCM showed a chemically reversible reduction wave at –1.20 V on the timescale of the experiment (Fig. 3d). The reversibility of the first reduction wave observed in **4b** suggested an increased stability of the transient $[(NMe_2Ar\text{-}BIAN)InCl_3]^-$ complex due to the stronger electron donation from **4a** to the metal center, thus, preventing dissociation of the Ar-BIAN ligand upon reduction. This is consistent with our previous observations on the voltammogram recorded for **6** bearing electron donating -OMe groups. Compound **6** also showed an electrochemically reversible reduction wave at –1.46 V, which was attributed to the stronger electron donation from the corresponding -OMe substituted ligand to the indium(III) center.[50] Although the assignment of each reduction and oxidation processes in **1b** to **4b** was hampered by the complex processes at the electrode surface, the redox behavior of **1b** to **4b** indicate that mild reducing agents with potentials between –1.0 V to –2.0 V can be utilized to effect reduction of the In(III) complexes.[62]

In view of this, the reduction of **1b** using magnesium anthracene was attempted in THF. Interestingly, based on the ^{1}H NMR spectra and visual observations of the reaction mixture, reduction of the Ar-BIAN ligand and the indium(III) nucleus appeared to occur concurrently. Indium metal deposition was observed from the reaction mixture and the protonated reduced Ar-BIAN ligand was the only isolated reaction product as indicated by a singlet at 5.06 ppm (SI, Fig. S11). This chemical shift corresponds to the two N-H bonds of a reduced Ar-BIAN ligand, which matches the spectrum obtained from an independent reduction of ligand **1a**. Similarly, reduction reactions of **6** using $CoCp_2$ resulted in formation of the reduced Ar-BIAN ligand MeOAr-BIAN-H_2 (**8**). The presence of **8** was confirmed by ^{1}H NMR spectroscopy[63] and single crystal X-ray diffraction (SI Fig. S12). The observed formation of the reduced ligand in the attempted reduction reactions of **1b** and **6** may be attributed to the redox non-innocence of the Ar-BIAN ligands. As mentioned in the Introduction, it has been demonstrated that reduction reactions sometimes occur on the diimine ligand rather than the metal center among both main group[64-65] and transition metal complexes.[1, 66] Future studies will involve the use of: (i) bulkier aryl substituents to kinetically stabilize the indium(I) products, which has been successfully adopted for indium(I) complexes comprising redox innocent ligands;[67] (ii) more electron-rich aryl substituents to preclude electron transfer from the indium(I) center to the Ar-BIAN ligand; and (iii) ligands and solvents of different electronic properties to stabilize the heteroleptic indium(I) center. Studies involving these approaches are currently undergoing.

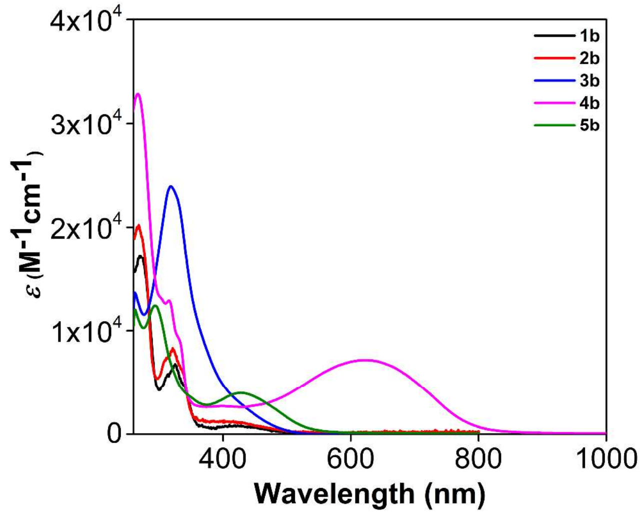


Figure 2. UV-vis spectra for **1b** and **2b** in THF, **3b** and **5b** in DMF, and **4b** in DCM solution. All solutions were prepared, each with a concentration of 0.10 mM.

Table 1. Electrochemical data for **1b** to **4b**

	Potential (V vs. Fc$^+$/Fc)	
	Cathodic peaks	Anodic peaks
1b	-1.61	-2.72
	-1.87	-2.26
	-2.41	-1.75
	-2.95	-0.54
		+0.22
2b	-1.14	-2.57
	-1.61	-2.11
	-2.30	-1.38
	-2.84	-0.98
		-0.42
3b	-1.25	-2.14
	-1.97	-1.64
	-2.32	-1.21
	-2.49	-0.08
		+0.51
4b	+0.28	-1.47
	-0.06	-1.15
	-1.24	-0.72
	-1.62	+0.44
	-1.85	+0.64

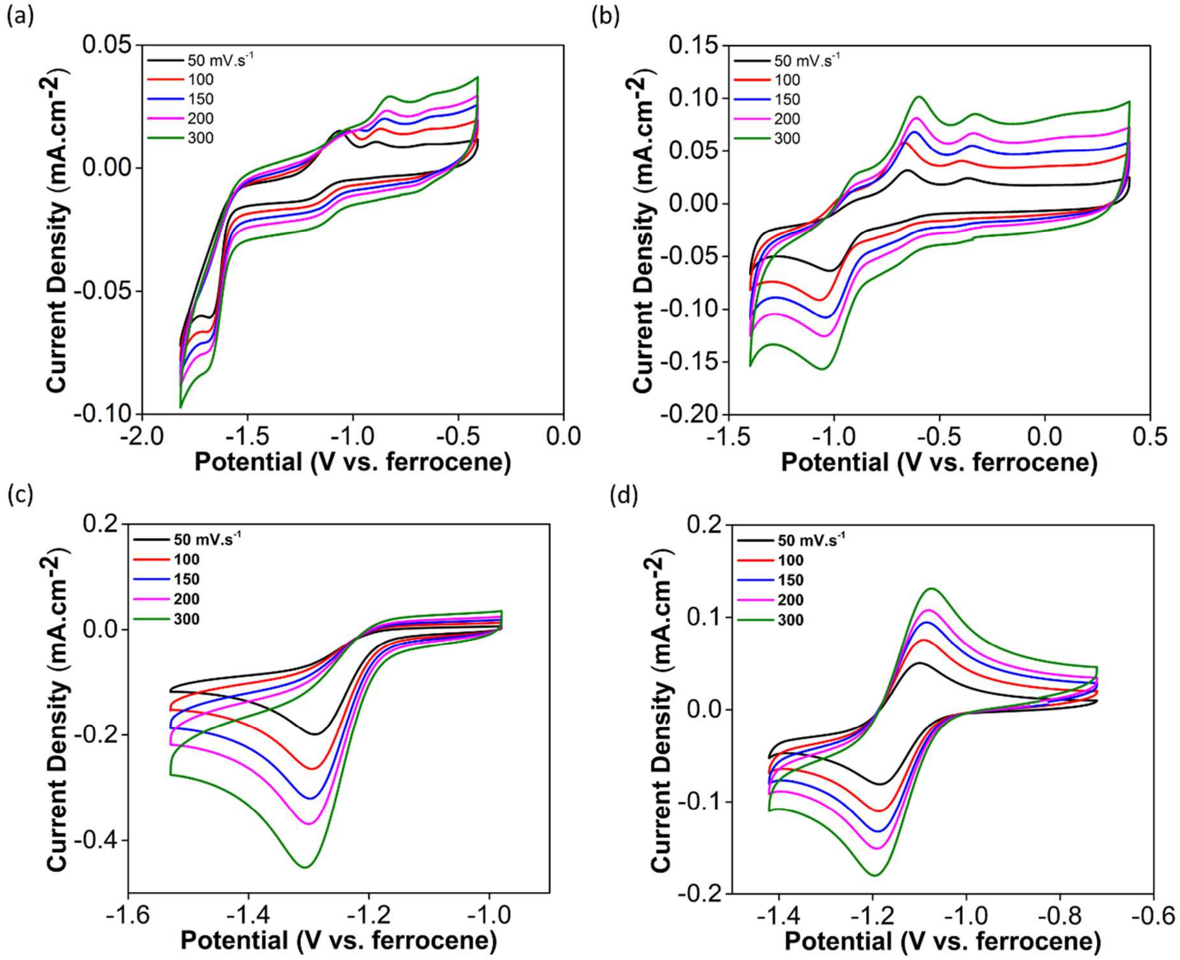


Figure 3. Cyclic voltammograms of the first reduction wave for **1b** (a) in THF, **2b** (b) in THF, **3b** (c) in DMF, and **4b** (d) in DCM solution at 298 K with 0.10 M $(nBu_4N)PF_6$ as the supporting electrolyte and glassy carbon (3 mm in diameter) as the working electrode. Data were collected using scan rates ranging from 50 to 300 mV.s^{-1} and all potentials reported were referenced to Fc^+/Fc.

Computational studies

DFT and TD-DFT calculations were undertaken to predict the electronic absorption spectra of the complexes described herein. The geometry of each complex was optimized with the hybrid functional B3LYP/6-31+G*, using the pseudo potential LANL2DZ basis set for the indium and chlorine atoms. A larger basis set 6-31++G* was used for our previously reported complexes **6** and **7**, with almost identical outcomes as the ones obtained from the basis set 6-31+G*. Hence, all geometry optimizations were carried out with the smaller 6-31+G* basis set in this article since it would be computationally cheaper. The optimized ground state structures for all complexes agreed closely with our X-ray crystallographic studies. Each optimized structure of **1b** and **2b** displays a plane of symmetry bisecting the acenaphthene and indium metal center. The frontier orbitals illustrating the electron density distribution for **1b** to **4b** are shown in Fig. 4. For **1b**, **2b**, and **4b**, the HOMO is mostly distributed on the di(arylimine) part of the Ar-BIAN ligand, while the LUMO is mainly localized on the acenaphthene moiety. However, for **3b**, the HOMO is localized on the acenaphthene bay region, whereas the LUMO has distributed contributions throughout the entire ligand. This intriguing reversal in orbital density when strongly electron-withdrawing groups are installed on the di(arylimine) motif is consistent with previous DFT calculations performed on a series of Ar-BIAN ligand by Zysman-Colman and coworkers.[14] From the TD-DFT analysis, the absorption maxima in **1b** and **2b** (λ_{max} = 320 nm) are mainly attributed to electronic transitions from the HOMO-3 → LUMO+1, while for **3b** (λ_{max} = 318 nm), it corresponds largely to a combination of the HOMO → LUMO+3, HOMO-1 → LUMO+2, and HOMO-8 → LUMO transition (SI, Tables S32-S34). In the case of **4b**, the calculated predominant contribution to the lower energy absorption maximum (λ_{max} = 630 nm) corresponds exclusively to the HOMO→LUMO transition, whereas the higher energy UV absorption band (λ_{max} = 267 nm) consists of a combination of contributions from HOMO-14→LUMO, HOMO-15→LUMO, and HOMO→LUMO+7 transitions (SI, Table S35).

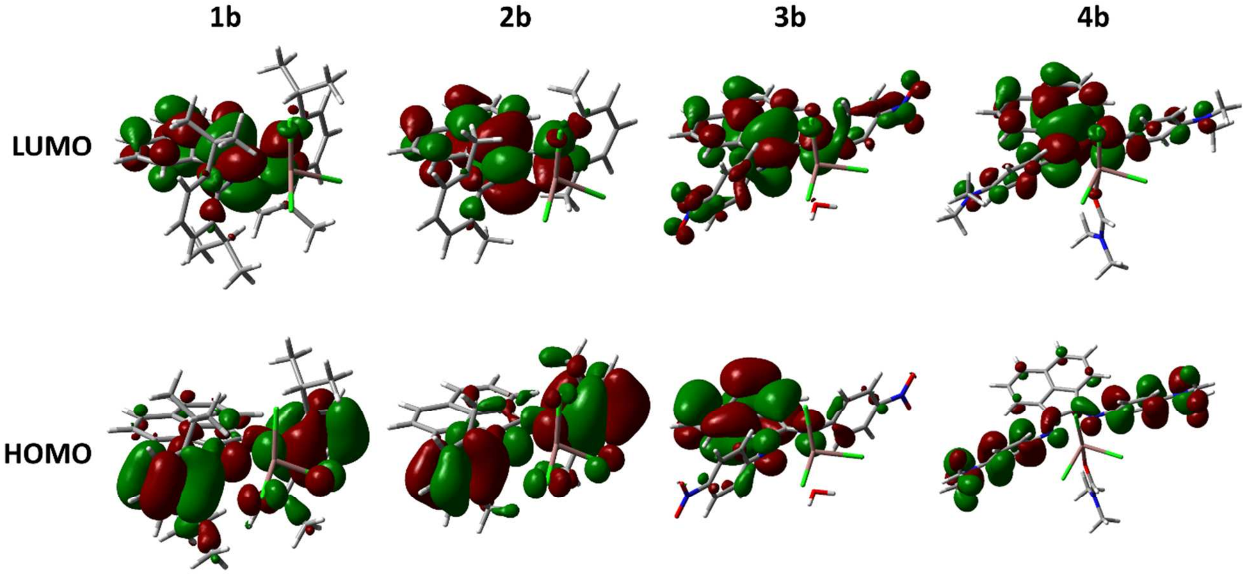


Figure 4. Electron density distributions of the frontier orbitals for **1b** to **4b**.

CONCLUSIONS

We have conducted a comprehensive investigation on the synthesis, absorption, and electrochemical properties of a series of five indium(III) complexes bearing redox non-innocent Ar-BIAN ligands. All the complexes within this study absorb light over wavelengths ranging from 380 – 800 nm, with **4b** absorbing furthest to the red region, which can be attributed to the small HOMO-LUMO gap due to the -NMe_2 substituent. On the other hand, the absorption spectrum of **3b** revealed a single intense band at 320 nm resulting from enlarged frontier orbital energy gaps arising from the electron withdrawing -NO_2 group. The CVs showed irreversible reduction waves ranging from -1.2 to -1.9 V for compounds **1b** – **3b**, whereas this reduction was observed to be chemically reversible for compound **4b** and our previously reported complex **6**. Although disproportionation and ligand reduction were observed during our attempted reduction of **1b** and **6**, we ascribe it to the non-innocent behavior of the Ar-BIAN ligand, which can accommodate the extra electrons more readily than the In metal center. Future work will involve modifying both the steric and electronic properties of the Ar-BIAN ligands, as well as using different counter anions and ligands in heteroleptic systems to prevent electron transfer from the metal to the Ar-BIAN ligand.

EXPERIMENTAL DETAILS

General procedures

All reactions with $InCl_3$ and the recrystallization of products were performed under dry and inert atmospheres by using a combination of standard Schlenk line techniques and a Vacuum Atmospheres Company N_2 glovebox. Solvents including tetrahydrofuran (THF), diethyl ether (Et_2O), and pentane were distilled over Na/benzophenone and degassed using freeze-pump-thaw cycles prior to use. Anhydrous acetonitrile (ACN) was collected from a PURE SOLV MD-5 solvent purification system and stored in a glovebox. Anhydrous 1, 2-dimethoxyethane (DME) and dichloromethane (DCM) were distilled over calcium hydride (CaH_2) and stored in a glovebox. Anhydrous N,N-Dimethylformamide (DMF) in a Sure-Seal bottle was purchased from Sigma-Aldrich and used as received. Deuterated chloroform ($CDCl_3$) and acetonitrile (CD_3CN) were distilled over CaH_2 and stored over 4 Å molecular sieves. Deuterated acetone was distilled over potassium carbonate (K_2CO_3). All reagents were purchased from commercial sources and were used without further purification. Synthetic procedures for **6** and **7** were reported by our team previously.[50] The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 298 K on Bruker AV400 and BBFO 400 spectrometers. The chemical shift values are reported in parts per million (ppm) relative to TMS, using residual protonated solvents as the internal standards (^1H: $\delta = 7.26$ for $CDCl_3$ and $\delta = 1.94$ for CD_3CN; ^{13}C: $\delta = 77.2$ for $CDCl_3$, and $\delta = 118.3$ for CD_3CN). The ^{115}In NMR data have not been reported due to the large quadrupolar moments of the nuclei, which result in broad and essentially unobservable NMR signals in the solid-state.[68-70] This is especially the case due to the low symmetry of our reported complexes.

Other Instrumentation

High-resolution mass spectra were obtained by using a Waters Q-Tof Premier, with ESI mode. Crystallographic data were recorded on a Bruker X8 CCD diffractometer. UV-vis spectroscopic measurements were performed using a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer. Cyclic voltammetry (CV) experiments were conducted in a glovebox with N_2 atmosphere, using a Biologic SP-300 potentiostat with 1.0 mM solutions of each sample and 0.10 M of tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as the electrolyte. Melting points were measured on an OptiMelt automated melting pointing system using sealed glass capillaries under argon and were uncorrected.

Synthesis of indium(III) complexes

(dipp-BIAN)InCl$_3$ (1b): A solution of $InCl_3$ (0.025 g, 0.11 mmol) in THF (5 mL) was added to a solution of dipp-BIAN (0.056 g, 0.11 mmol) in THF (5 mL) at room temperature. (see Supporting Information, SI, for synthesis of dipp-BIAN) The resulting orange solution was stirred overnight, after which all volatiles were removed under vacuum. The resultant orange powder was recrystallized by vapor diffusion of pentane into a DME solution of the crude product and the isolated yield was 0.061 g (76%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (d, $J = 7.2$ Hz, 12 H), 1.38 (d, $J = 6.8$ Hz, 12 H), 3.07 (sept, $J = 6.8$ Hz, 4 H), 6.75 (d, $J = 7.2$ Hz, 2 H), 7.40 (d, $J = 7.6$ Hz, 4 H), 7.50-7.54 (m, 2 H), 7.60 (t, $J = 8.0$ Hz, 2 H), 8.17 (d, $J = 8.0$ Hz, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 24.4$, 24.8, 29.9, 125.1, 126.2, 127.8, 129.1, 129.3, 131.1, 133.2, 140.0, 140.3, 144.3, 162.7. m.p.: decomposed at 280°C HRMS (ESI+, m/z) calculated for

$C_{36}H_{40}N_2InCl_3Na$ $[M+Na]^+$ *m/z* = 743.1194, found 743.1179. Anal. Calcd. for $C_{36}H_{40}N_2InCl_3$: C, 59.90; H, 5.59; N, 3.88. Found: C, 59.56; H, 5.43; N, 3.82.

(2,6-Me$_2$Ar-BIAN)InCl$_3$ (2b): The procedure was identical to the one reported above for **1b**. The following quantities of reagents were used: $InCl_3$ (0.023 g, 0.10 mmol) in THF (5 mL), 2,6-Me$_2$Ar-BIAN (0.040 g, 0.10 mmol) in THF (5 mL). (see SI for synthesis of 2,6-Me$_2$Ar-BIAN) Orange block-like crystals suitable for single crystal X-ray analysis were obtained by recrystallization via vapor diffusion of pentane into a THF solution of the crude product and the isolated yield was 0.026 g (41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 12 H), 6.79 (d, *J* = 7.2 Hz, 2 H), 7.28-7.30 (m, 4 H), 7.33-7.37 (m, 2 H), 7.62 (t, *J* = 7.8 Hz, 2 H), 8.21 (d, *J* = 8.4 Hz, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.0, 125.8, 126.7, 128.4, 129.6 (two overlapping signals), 129.9, 131.1, 133.5, 142.1, 144.6, 162.3. m.p.: decomposed at 273°C HRMS (ESI+, *m/z*) calculated for $C_{28}H_{24}N_2InCl_3Na$ $[M+Na]^+$ *m/z* = 630.9942, found 630.9954. Anal. Calcd. for $C_{28}H_{24}N_2InCl_3\cdot THF\cdot H_2O$: C, 54.92; H, 4.90; N, 4.00. Found: C, 55.16; H, 4.93; N, 4.26.

(*p*-NO$_2$Ar-BIAN)InCl$_3$ (3b): The procedure was similar to the one reported above for complex **1b** except that this reaction was carried out under reflux conditions overnight. The following quantities of compounds were used: $InCl_3$ (0.044 g, 0.20 mmol) and *p*-NO$_2$Ar-BIAN (0.084 g, 0.20 mmol) in THF (7 mL). (see SI for synthesis of *p*-NO$_2$Ar-BIAN) The resultant yellow solid was purified by washing with THF and the isolated yield was 0.083 g (64%). The purity of the product was confirmed by elemental analysis. Yellow block-like crystals suitable for single crystal X-ray analysis were obtained by recrystallization from an ACN solution of the crude product. ^{1}H NMR (400 MHz, acetone-d$_6$): δ = 7.27 (d, *J* = 6.8 Hz, 2 H), 7.75-7.79 (m, 6 H), 8.44 (d, *J* = 8.4 Hz, 2 H), 8.55-8.58 (m, 4 H). The $^{13}C\{^1H\}$ NMR could not be obtained due to the poor solubility of **3b** in most of the available deuterated solvents. m.p.: decomposed after 320°C HRMS (ESI+, *m/z*) calculated for $C_{24}H_{14}Cl_3InN_4O_4Na$ $[M+Na]^+$ *m/z* = 664.9017, found 664.9005. Anal. Calcd. for $C_{24}H_{14}Cl_3InN_4O_4{\cdot}THF$: C, 46.99; H, 3.10; N, 7.83. Found: C, 46.63; H, 3.45; N, 8.15.

(*p*-NMe$_2$Ar-BIAN)InCl$_3$ (4b): The procedure was identical to the one reported above for **1b.** The following quantities of reagents were used: $InCl_3$ (0.066 g, 0.30 mmol) in THF (5 mL), *p*-NMe$_2$Ar-BIAN (0.130 g, 0.30 mmol) in THF (5 mL). (see SI for synthesis of *p*-NMe$_2$Ar-BIAN) The purple solution was stirred overnight, after which all volatiles were removed under vacuum. The resultant deep blue solid was washed with Et_2O. Purple needle-like crystals suitable for single crystal X-ray analysis were obtained from recrystallization by vapor diffusion of Et_2O into a DMF solution of the crude product and the isolated yield was 0.13 g (68%). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C, *fac*-isomer): δ = 3.09 (s, broad, 12 H), 6.88 (d, J = 9.2, 2 H), 7.04-7.06 (m, 4 H), 7.40 (d, J = 6.8, 2 H), 7.54-7.60 (m, 4 H), 8.17 (d, J = 8.0 Hz, 2 H) . $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 40.6, 40.7, 112.5, 123.0 (broad, may have peaks overlapping), 124.3, 126.1 (broad, may have peaks overlapping), 127.2, 128.8, 129.1, 131.3 (two peaks), 131.7, 132.8 (broad, may have peaks overlapping), 133.5, 143.8, 144.1, 150.9, 151.3 (broad, may have peaks overlapping), 157.7. m.p. 198-202°C HRMS (ESI+, *m/z*) calculated for $C_{31}H_{33}N_5InCl_3Na$ $[M+Na]^+$ *m/z* = 734.0687, found 734.0652. Anal. Calcd. for $C_{31}H_{33}N_5OInCl_3{\cdot}H_2O$: C, 50.95; H, 4.83; N, 9.58. Found: C, 50.90; H, 4.90; N, 9.32.

(*p*-MeOAr-BIAN)InCl$_3$•DMF (5b):[50] The synthetic procedure was reported in a recent publication by our team and it has been included here for completeness. Recrystallization by vapor diffusion of Et_2O into a DMF solution of the red solid resulted in samples suitable for single crystal X-ray analysis. ^1H NMR (400 MHz, CD_3CN, *fac*-isomer): δ = 3.92 (s, 6 H), 7.16-

7.18 (m, 4 H), 7.33-7.36 (m, 4 H), 7.56-7.65 (m, 4 H), 8.31 (d, *J* = 6.8 Hz, 2 H). ^{13}C{^{1}H}3.33 NMR (100 MHz, DMF-d_7): δ = 56.4, 114.4, 115.8, 116.0, 119.9, 120.4 (broad overlapping peaks), 122.8, 124.3 (broad overlapping peaks), 124.6, 127.2 (broad overlapping peaks), 129.0 (broad overlapping peaks), 130.1, 130.3, 133.5, 138.7, 158.1, 160.6. HRMS (ESI+, *m/z*) calculated for $C_{29}H_{27}Cl_3InN_3O_3Na$ [M+Na]$^+$ *m/z* = 708.0054, found 708.0081. Anal. Calcd. for $C_{29}H_{27}N_3O_3InCl_3 \cdot H_2O$: C, 49.43; H, 4.15; N, 5.96. Found: C, 49.84; H, 4.55; N, 6.12.

Reduction of [(*p*-MeOAr-BIAN)$_2$InCl$_2$]$^+$[InCl$_4$]$^-$ (6): A THF solution (5 mL) of $CoCp_2$ was added dropwise to a THF suspension (5 mL) of **6** at room temperature. The resulting brown suspension was stirred for 2 h, after which all volatiles were removed under vacuum. The crude purple solid was washed with Et_2O and the purple filtrate was filtered and concentrated. The ^{1}H NMR experiments were conducted on the resultant purple solid. ^{1}H NMR (400 MHz, C_6D_6): 3.33 (s, 6 H), 4.93 (s, 2 H), 6.72-6.77 (m, 8 H), 7.12-7.42 (m, overlapping with signal from C6D6), 7.43 (d, *J* = 8.0 Hz, 2 H).

Theoretical basis

DFT calculations were used to evaluate both the geometries and energies of the different indium complexes possessing one or two coordinated Ar-BIAN ligands. The initial energy and geometry optimization was carried out at the B3LYP[71-73] level with the 6-31+G* basis set for non-metal atoms[74], together with the pseudo potential LANL2DZ[75] for the In and Cl atoms. The agreement between the experimentally determined and the computed structures supports the method used. Frequency calculations were carried out at this level to confirm that a minimum had been achieved. To account for solvent effects, a reaction field calculation with radii and nonelectrostatic terms and the SMD solvation model was used.[76] All the TD-DFT calculations were carried out using the Gaussian 09 program package.[71-73, 77]

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ASSOCIATED CONTENT

Supporting Information. General procedures, experimental details, photophysical and electrochemical characterization protocols, ^{1}H and ^{13}C NMR spectra, crystallographic data (CCDC 1535077-1535081) and computational details. This material is available free of charge via the Internet at http://pubs.acs.org with DOI: 10.1021/acs.inorgchem.XXXXXXX.

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60. Despite the synthesis of 5b being reported in our previous study, its structural features when crystallized in N,N-dimethylformamide (DMF) is discussed in the present paper.

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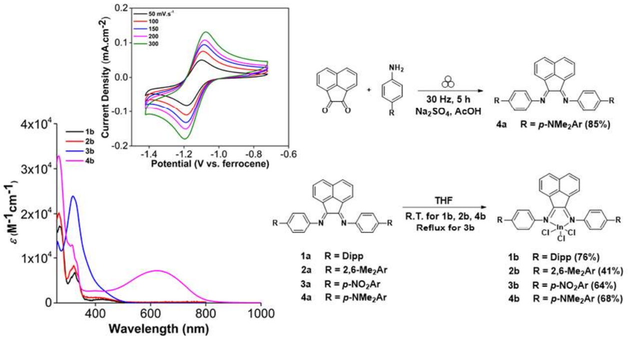
TOC graphic "For Table of Contents Only"

The synthesis and spectroscopic studies of four new indium(III) Ar-BIAN complexes, bearing 2,6-dialkyl (**1b** and **2b**), 4-nitro (**3b**), and 4-dimethylamino groups (**4b**) at the aryl-diimine part of the ligand are reported and DFT calculations have been performed to gain insights into the nature of the optical properties displayed.



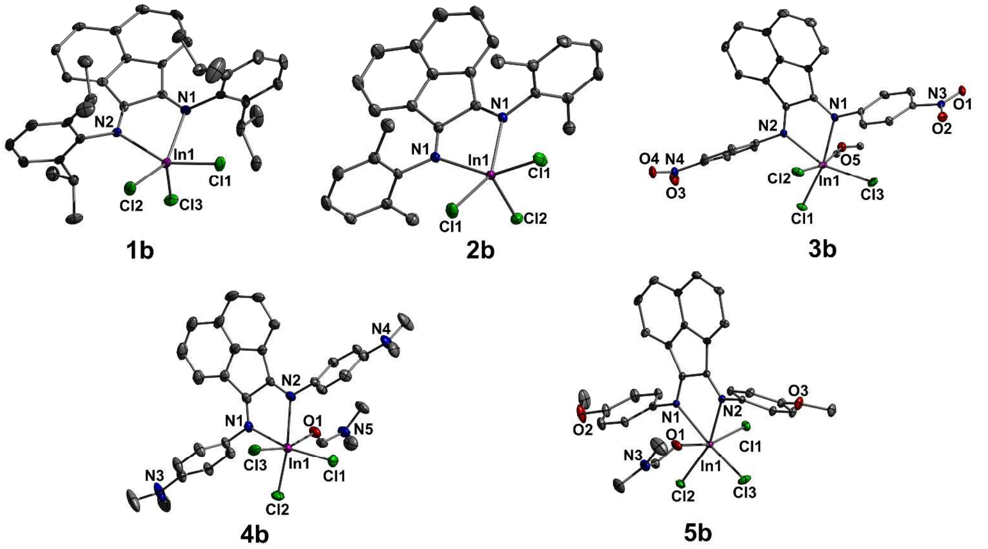


Figure 1. Selected bond lengths (Å) and angles (°) of complexes (1b) In1-N1 2.342(5), In1-N2 2.339(5), In1-Cl1 2.3835(16), In1-Cl2 2.3800(17), In1-Cl3 2.3643(17); (2b) In1-N1 2.3196(15), In1-Cl1 2.3897(5), In1-Cl2 2.3769(7); (3b) In1-N1 2.3230(14), In1-N2 2.3114(14), In1-Cl1 2.4013(4), In1-Cl2 2.4722(5), In1-Cl3 2.4032(5), In1-O5 2.2733(13); (4b) In1-N1 2.317(3), In1-N2 2.331(3), In1-Cl1 2.4029(10), In1-Cl2 2.4241(9), In1-Cl3 2.4408(10), In1-O1 2.259(3); (5b) In1-N1 2.3182(14), In1-N2 2.3444(13), In1-Cl1 2.4417(4), In1-Cl2 2.4301(4), In1-Cl3 2.4058(5), In1-O1 2.2306(13). Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

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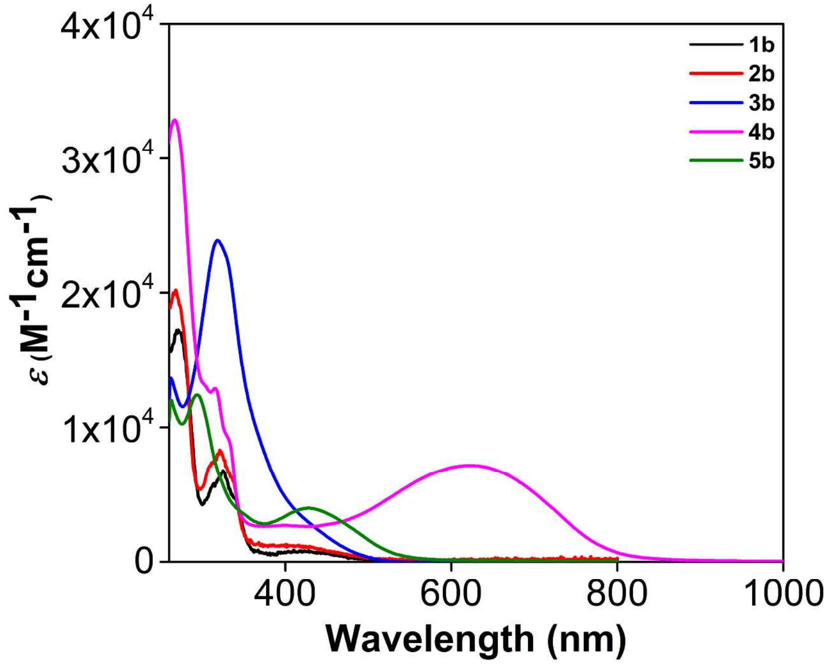

Figure 2. UV-vis spectra for 1b and 2b in THF, 3b and 5b in DMF, and 4b in DCM solution. All solutions were prepared, each with a concentration of 0.10 mM.

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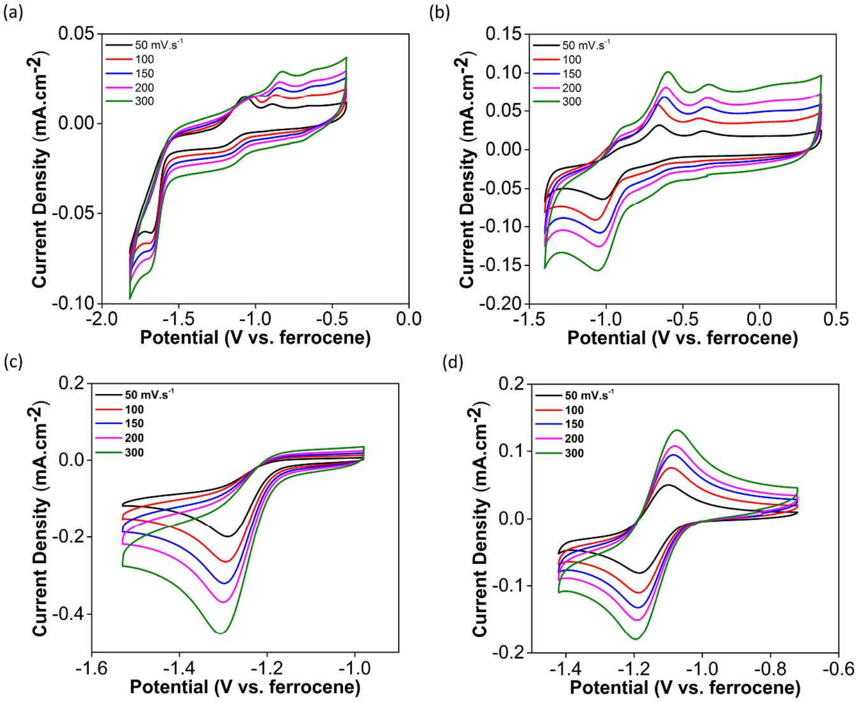

Figure 3. Cyclic voltammograms of the first reduction wave for 1b (a) in THF, 2b (b) in THF, 3b (c) in DMF, and 4b (d) in DCM solution at 298 K with 0.10 M (nBu4N)PF6 as the supporting electrolyte and glassy carbon (3 mm in diameter) as the working electrode. Data were collected using scan rates ranging from 50 to 300 mV.s-1 and all potentials reported were referenced to Fc+/Fc.

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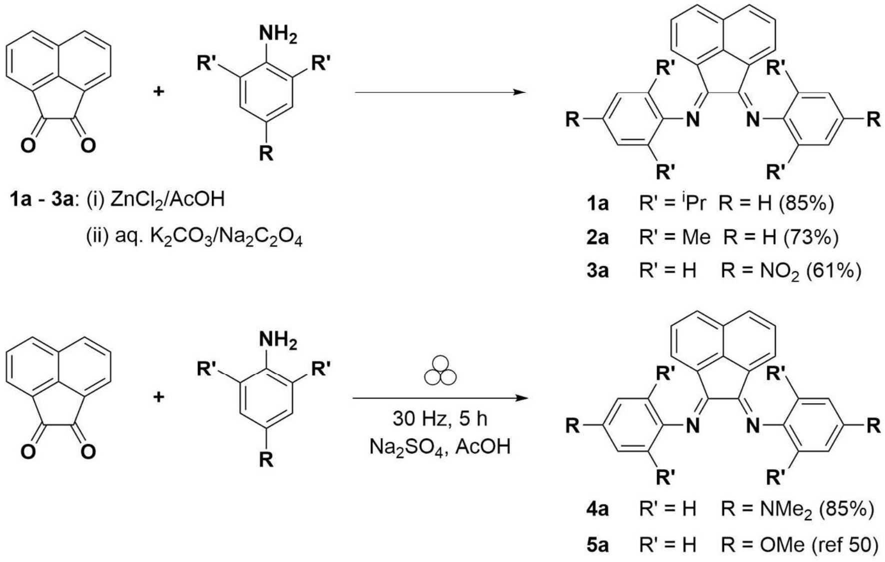

Scheme 1 General synthetic scheme of Ar-BIAN ligands 1a – 5a. The symbol for mechanical milling above the arrow of the equation in the lower half has been proposed by Hanusa et al.58

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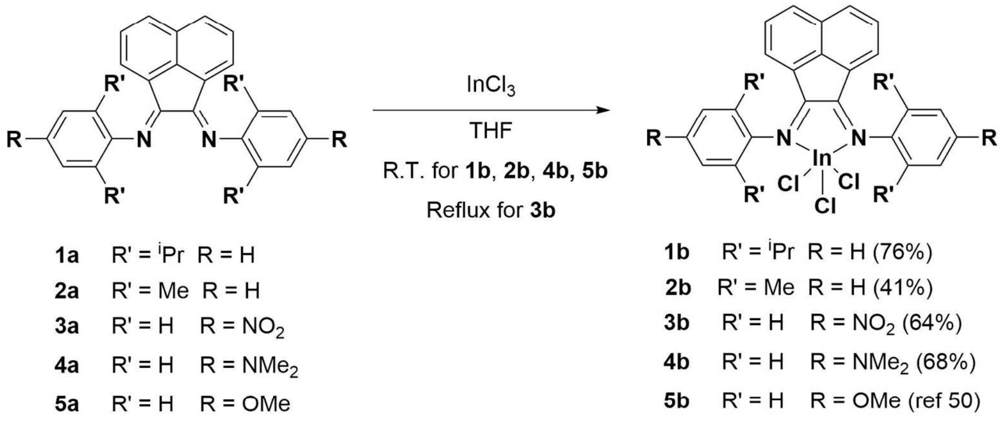

Scheme 2 Synthetic route to 1b – 5b.

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