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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

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3 UV-vis spectroscopy and cyclic voltammetry, respectively. Additionally, DFT calculations were
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5 performed to gain insights into the nature of the properties displayed.
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8 9 INTRODUCTION

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12 Redox processes and redox-active ligands play important roles in modern chemical
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14 transformations constituting exciting areas of research in coordination and organometallic
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16 chemistry,¹ and catalysis.² The term “*innocent ligand*” was first coined by Jørgensen as a ligand
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18 that allows the oxidation states of the central atoms to be readily determined.³ In contrast, “*non-*
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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

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3 the preparation of numerous transition metal molecular compounds, which could be of use in
4 photosensitization applications due to the characterized MLCT (metal-to-ligand charge transfer)
5 transition from the d-orbitals of the transition metal to the π^* orbitals of the Ar-BIAN ligand.^{9-10,}
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10 ¹⁶ The low-lying π^* orbitals of Ar-BIAN ligands have been successfully exploited as ‘capacitors’
11 for multi-electron reductions in redox non-innocent ligands.¹⁷⁻¹⁹ Consequently, there have been
12 reports of transition metal Ar-BIAN complexes being used as catalysts for organic reactions such
13 as cycloaddition of azides and alkynes,⁷⁻⁸ as well as olefin polymerization, work that had been
14 pioneered by M. Brookhart and coworkers using Ni(II) and Pd(II) Ar-BIAN complexes.²⁰⁻²⁷
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17 More recently, Cu(II) Ar-BIAN complexes have been investigated as catalysts for the reverse
18 atom transfer radical polymerization (ATRP) of styrene.²⁸ Moreover, applications of Cu(I) Ar-
19 BIAN complexes as light harvesters that can absorb to the NIR region have also been reported.^{6,}
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32 In terms of main group chemistry, however, groups 1 and 2 constitute majority of the Ar-BIAN
33 main group metal complexes.^{17-19, 29-35} In these examples, each Ar-BIAN ligand undergoes facile
34 reduction due to its electron accepting nature to form the corresponding metal complex.¹¹ With
35 respect to Group 14 metals, a small number of complexes have been previously reported. For
36 instance, *N*-heterocyclic germylenes that contain anionic Ar-BIAN ligands include [(dipp-
37 BIAN)Ge:], [(dtb-BIAN)Ge:] (dipp = 2,6-diisopropylphenyl, dtb = 2,5-(*t*-Bu)₂Ph), and [(bph-
38 BIAN)Ge:] (bph = (2-PhC₆H₄)).³⁶ Moreover, complexes such as (dipp-BIAN)GeCl have been
39 prepared by reacting the neutral Ar-BIAN ligands with GeCl₂, where the GeCl₂ acts as a
40 reducing agent for the Ar-BIAN ligands to form their radical anionic counterparts.³⁷⁻³⁸ On going
41 down this group, tin complexes supported by neutral Ar-BIAN ligands have also been described,
42 including [(mes-BIAN)SnCl₄] (mes = 2,4,6-trimethylphenyl) and [(dtb-BIAN)SnCl₂].^{12, 38-39} A
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3 series of group 15 and 16 Ar-BIAN metal complexes have been previously characterized as well.
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5 For example, [(dipp-BIAN)SbCl₃ and [(mes-BIAN)BiCl₃]¹² supported by neutral Ar-BIAN
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7 ligands, and [(dipp-BIAN)E] [SnCl₅•THF] obtained by reduction of ECl₃ (E = P and As) with
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9 SnCl₂, followed by treatment with dipp-BIAN to give their dianionic form.⁴⁰ As for the
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11 chalcogens, the reaction of TeI₄ with neutral dipp-BIAN results in a two-electron reduction of
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13 the metal center to form [(dipp-BIAN)TeI₂], in which the ligand is neutral and the chalcogen has
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15 been reduced to the +2 oxidation state.⁴¹ More recently, the (dipp-BIAN)SeCl₂ and (dipp-
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17 BIAN)SeBr₂ counterparts have also been described.⁴² Clearly, the redox non-innocence of Ar-
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19 BIAN ligands have contributed to some rich chemistry and oxidation state ambiguity even
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21 among main group coordination compounds.
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28 In the case of group 13 complexes, other than a limited number of boron compounds,^{39,43} only a
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30 few aluminum and gallium Ar-BIAN complexes have been isolated and structurally
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32 characterized.⁴³⁻⁴⁹ In particular, until very recently,⁵⁰ there was only one crystallographically
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34 characterized example of a monometallic Ar-BIAN indium(III) complex,¹² and two reports
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36 presenting the related tetrakis(imino)py-racene (TIP) ligand.⁵¹ Hence, the synthesis of new,
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38 heavy group 13 Ar-BIAN complexes and the evaluation of their absorption and electrochemical
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40 properties still remain under-explored areas.
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46 Our group is interested in applying mechanochemical approach to synthetic main group
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48 compounds⁵² and has recently reported the preparation of new indium(III) bis(arylimino)-
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50 acenaphthene complexes by using an essentially solvent-free mechanochemical approach.⁵⁰ The
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52 indium(III) complexes were characterized by density functional theory (DFT) calculations,
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54 electrochemistry, and UV-Vis-NIR spectroscopy. The electrochemical data suggested that the
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56 Ar-BIAN indium(III) complexes could be converted to their indium(I) congeners by mild
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3 reducing agents, offering us the opportunity to explore the intriguing redox non-innocence of the
4 Ar-BIAN systems. Upon reduction of the indium(III) center, these complexes show potential for
5 applications as photosensitizers, dovetailing with our interest in the use of Earth-abundant
6 elements in artificial photosynthesis.^{16, 53-55}
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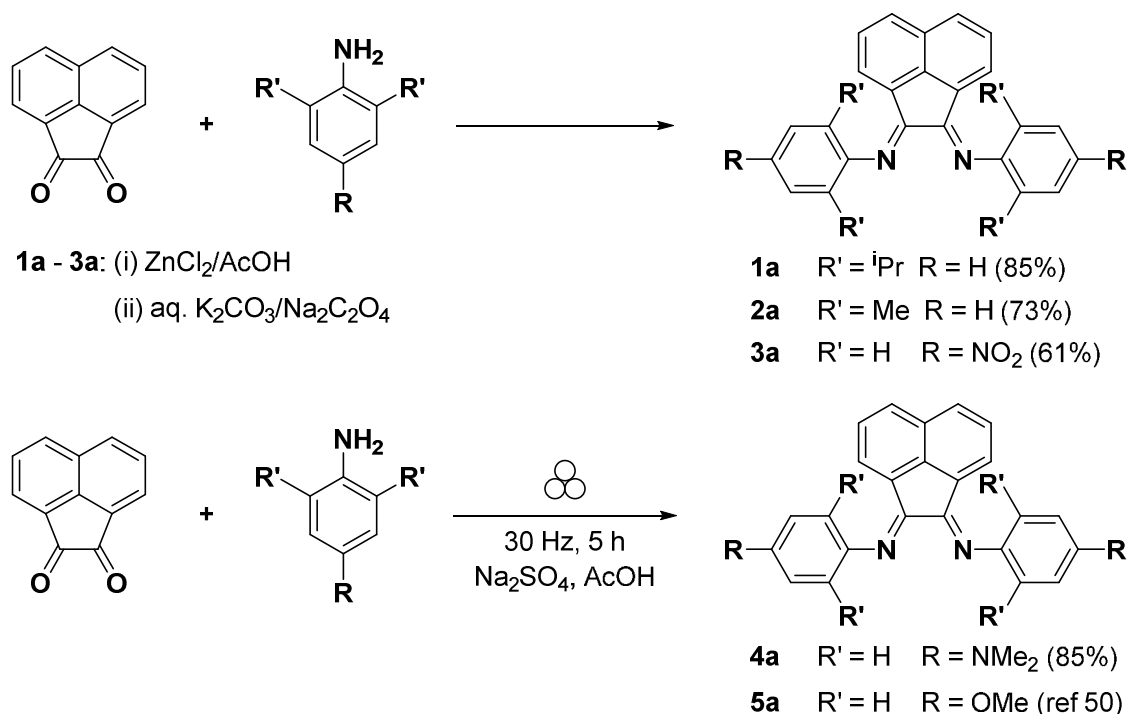
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13 Herein, we present a family of new indium(III) Ar-BIAN complexes with the synthesis of a
14 broad range of Ar-BIAN ligands comprising electron-donating and electron-deficient
15 substituents on the arylimino fragment. All of the complexes reported here have been structurally
16 characterized, and probed with electrochemical and UV-vis spectroscopic measurements, as well
17 as DFT and TD-DFT calculations.
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25 26 **RESULTS AND DISCUSSION**

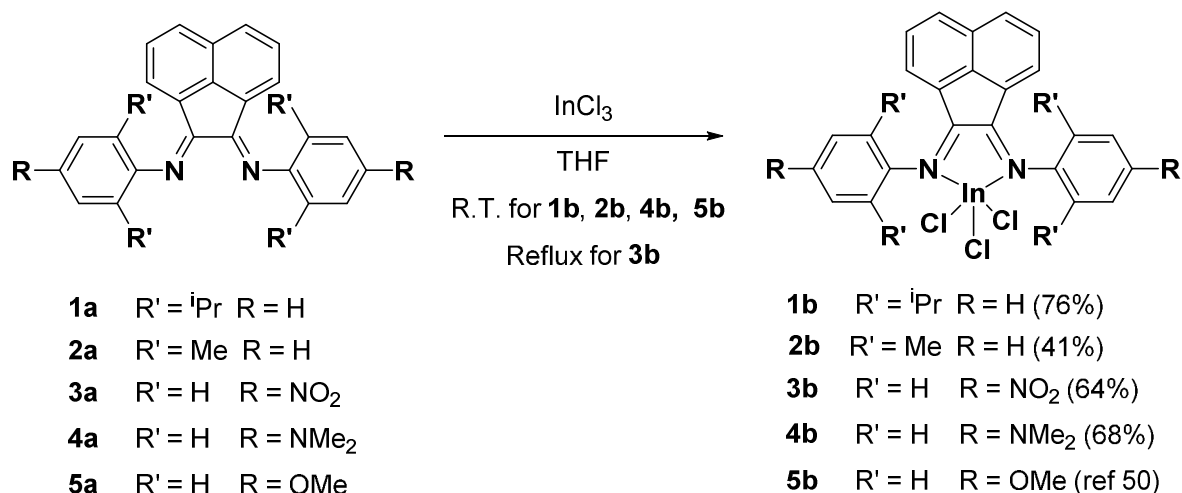
27 28 **Synthesis of complexes**

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32 The alkyl- and nitro-substituted Ar-BIAN ligands (**1a-3a**) were synthesized by
33 condensation of acenaphthoquinone with the corresponding aniline under acidic
34 conditions.⁵⁶⁻⁵⁷ The Lewis acidic ZnCl₂ was used as the templating agent, after which de-
35 metalation with K₂CO₃ or Na₂C₂O₄ was carried out (Scheme 1, top half). However, this
36 method proved unsuccessful for the synthesis of the *para*-amino-substituted **4a**, and
37 ligand hydrolysis was observed after the de-metalation step in an aqueous Na₂C₂O₄
38 solution. Alternatively, we have previously demonstrated that substituted Ar-BIAN
39 ligands can be successfully synthesized *via* mechanochemical methodologies, which
40 bypass the ZnCl₂ templating and subsequent de-metalation step.⁵⁰ Accordingly, **4a** was
41 prepared via a ball-milling mechanochemical approach in the presence of a catalytic
42 amount of acetic acid and Na₂SO₄ (Scheme 1, bottom half). The synthesis of **5a**, which
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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 ¹H NMR spectra, **4a** was formed with only trace amounts of unreacted precursors. Subsequent reaction of the Ar-BIAN ligand (**1a** – **5a**) with InCl₃ in tetrahydrofuran (THF) afforded the respective indium(III) Ar-BIAN complexes (**1b** – **5b**). The syntheses of **1b**, **2b**, **4b**, and **5b**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



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

Spectroscopic and Crystallographic Studies

The ¹H and ¹³C{¹H} NMR spectra obtained for **1b** to **5b** concurred with the formation of coordinated, neutral Ar-BIAN ligands on indium(III). In general, the ¹H 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 (Et₂O) into DMF. Therefore, the characteristic DMF signals were present in the ¹H NMR spectrum of **3b** recorded in deuterated acetone (SI, Fig. S5). In the case of **4b** and **5b**, vapor diffusion of Et₂O into DMF has been used for recrystallization and, hence, one DMF molecule is coordinated to each indium(III) metal center. Thus the ¹H 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*-

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3 MeOAr-BIAN)₂InCl₂]⁺[InCl₄]⁻ (**6**) and (*p*-BrAr-BIAN)InCl₃ (**7**), which we compare with and
4 refer to in this report for the completeness of our studies.⁵⁰ Compound [(*p*-MeOAr-
5 BIAN)₂InCl₂]⁺[InCl₄]⁻ (**6**) was originally recrystallized from ACN; however, when **6** is
6 recrystallized from a more strongly coordinating solvent like DMF, the mono Ar-BIAN complex
7 **5b** is formed. We attribute the formation of **5b** to the stronger coordinating ability of DMF
8 compared to ACN. Coordinating solvents (H₂O in **3b**, DMF in **4b** and **5b**) are bound to each
9 indium center resulting in distorted octahedral geometries for the complexes. The equatorial
10 bond angles range from 72.64(5)° to 101.06(2)° in **3b**, 72.85(10)° to 97.94(8)° in **4b**, and
11 72.68(5)° to 96.77(4)° in **5b**, deviating significantly from the ideal value of 90°. Similarly, the
12 axial bond angles (166.45(4)°, 164.01(7)°, and 162.18(4)° in **3b** to **5b**, respectively) also deviate
13 from the expected 180°. This deviation of axial and equatorial bond angles in a distorted
14 octahedral geometry was also reported in a similar mes-BIAN-InCl₃ complex.¹² In contrast, **1b**
15 and **2b** adopt distorted square pyramidal geometries presumably due to the increased steric
16 hindrance around the metal nucleus introduced by substitution of isopropyl (in **1b**) and methyl
17 (in **2b**) groups at the *ortho* positions of the aniline moiety. The axial bond angles range from
18 95.89(13)° to 110.12(6)° in **1b** and from 100.86(4)° to 107.42(19)° in **2b**, which are similar to
19 those in the related tetrakis(imino)pyracene (TIP) complexes that also adopt distorted square
20 pyramidal geometries around the indium center (94.2° – 117.4°).⁵¹ Complex **2b** exhibits a plane
21 of symmetry bisecting the acenaphthene fragment and the indium metal center, making the two
22 diimine N and Cl atoms at the equatorial positions equivalent. The C-C and C-N bond distances
23 within the diimine moiety in **1b** – **5b** (ranging from 1.517(3) Å to 1.535(8) Å and from 1.274(2)
24 Å to 1.288(4) Å, respectively) are consistent with typical of C-C and C=N bond lengths.¹²
25 Therefore, complexes **1b** – **5b** can be considered to consist of neutral Ar-BIAN ligands
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3 coordinated to indium(III) *via* dative bonds. The average In-N bond distances for **1b** and **2b**
4 (2.341 Å and 2.320 Å, respectively) are slightly shorter than their mes-BIAN-InCl₃¹² and the
5 dipp-TIP-InCl₃ counterparts (2.35 Å and 2.38 Å).⁵¹ The introduction of an electron withdrawing
6 -NO₂ group (in **3b**) and electron donating -NMe₂ (in **4b**) and -OMe groups (in **5b**) did not affect
7 the average In-N bond distances greatly. Their average In-N bond distances (2.317 Å in **3b**,
8 2.324 Å in **4b**, and 2.331 Å in **5b**) remained similar to that for **1b** and **2b**. Notably, complexes **1b**
9 to **5b** all exhibit In-Cl bond distances significantly longer than that for InCl₃(THF)₂ (2.331(3)
10 Å).⁶¹ The In-Cl bond distances in **1b** and **2b** range from 2.3643(17) to 2.3897(5) Å and are
11 shorter than those in the related mes-BIAN-InCl₃, likely due to the increased electron donation
12 from the mes-BIAN ligand in the latter, resulting in a weakening of the In-Cl bonds.¹² Although
13 **4b** and **5b** bear ligands that are more electron-rich than **3b**, the average In-Cl bond distances in
14 these complexes are similar (2.425 Å, 2.423 Å and 2.426 Å in **3b**, **4b**, and **5b** respectively).
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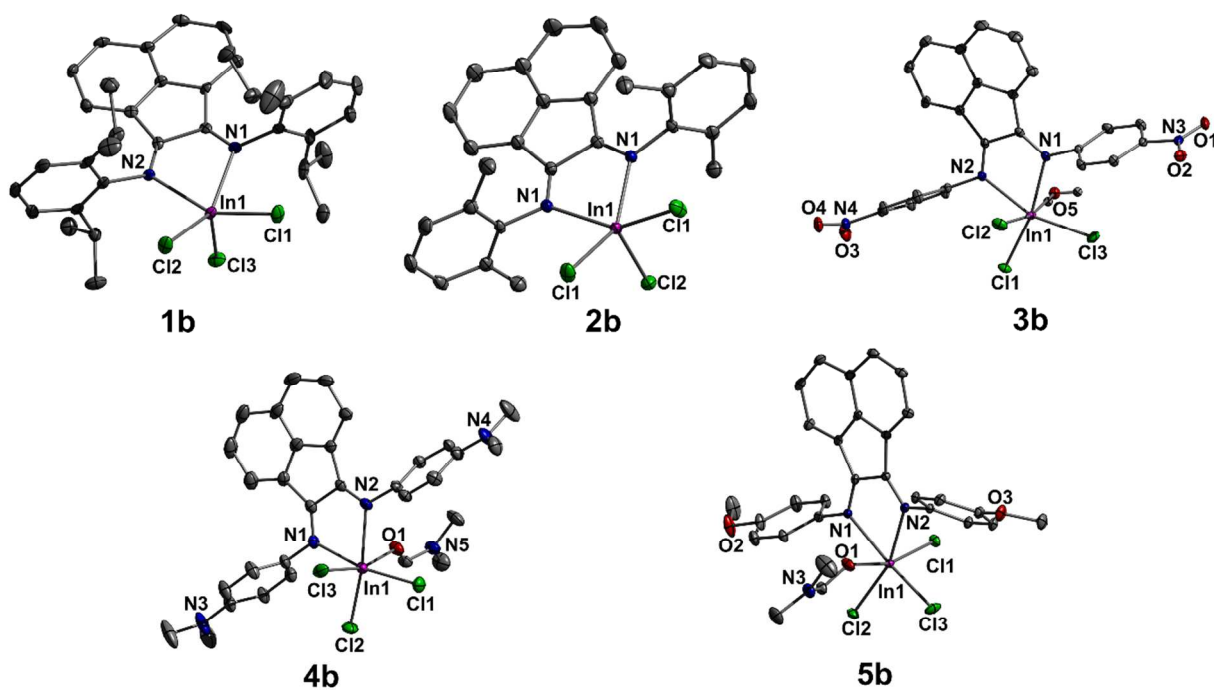


Figure 1. Selected bond lengths (Å) and angles (°) of complexes (**1b**) In1-N1 2.342(5), In1-N2 2.339(5), In1-C11 2.3835(16), In1-C12 2.3800(17), In1-C13 2.3643(17); (**2b**) In1-N1 2.3196(15), In1-C11 2.3897(5), In1-C12 2.3769(7); (**3b**) In1-N1 2.3230(14), In1-N2 2.3114(14), In1-C11 2.4013(4), In1-C12 2.4722(5), In1-C13 2.4032(5), In1-O5 2.2733(13); (**4b**) In1-N1 2.317(3), In1-N2 2.331(3), In1-C11 2.4029(10), In1-C12 2.4241(9), In1-C13 2.4408(10), In1-O1 2.259(3); (**5b**) In1-N1 2.3182(14), In1-N2 2.3444(13), In1-C11 2.4417(4), In1-C12 2.4301(4), In1-C13 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

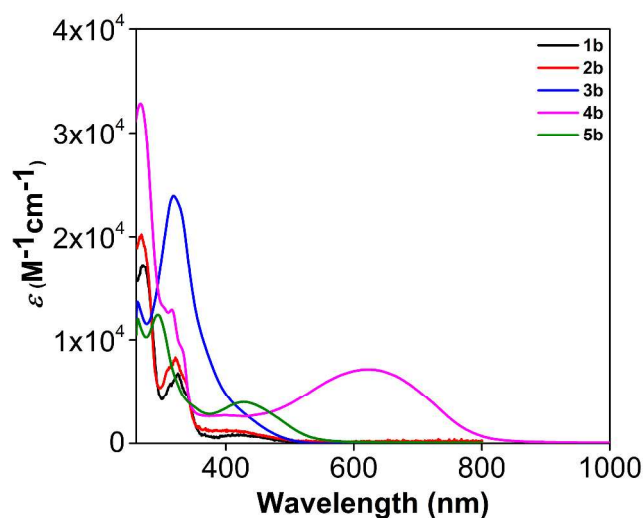
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3 introduced.¹⁴ The single intense absorption band at *ca.* 320 nm in **3b** may result from a
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5 coincidental convergence of multiple intraligand charge transfer transitions.
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9 With an initial objective to identify a suitable reducing agent with an adequate reduction
10 potential to obtain the indium(I) counterparts of complexes **1b** to **4b**, their redox properties were
11 examined by cyclic voltammetry. The redox potentials of accessible reduction and oxidation
12 waves are summarized in Table 1. The voltamogram for **5b** has not been collected in this report
13 since its redox potential is expected to be identical to the previously reported compound **6**, which
14 has been recorded in ACN. Since the molecular structures of **5b** and **6** are solvent dependent,
15 their redox potentials would be affected by the solvent used.⁵⁰ All potentials are reported relative
16 to the ferrocenium/ferrocene (Fc⁺/Fc) redox couple. A direct comparison of the voltamograms of
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18 **1b** to **4b** cannot be made due to their disparate solubility properties and the differences in their
19 coordination spheres. However, it is worth noting that the electrochemical behavior of **1b**, **2b**,
20 and **3b** consist of four irreversible reductions and a series of oxidations (Fig. 3). The
21 irreversibility may stem from the following. Firstly, detachment of a chloride ligand or
22 coordination of a solvent molecule to the indium species formed during the voltammetric sweep
23 may occur, since the reduction of the indium(III) center may involve structural changes arising
24 from the anion dissociation. Secondly, the ligand itself may reduce due to its non-innocent
25 nature. Thirdly, the putative indium(I) intermediates formed at the electrode surface may
26 disproportionate, which is also supported by the experimental findings (*vide infra*). In contrast,
27 the electrochemical behavior of **4b** in DCM showed a chemically reversible reduction wave at –
28 1.20 V on the timescale of the experiment (Fig. 3d). The reversibility of the first reduction wave
29 observed in **4b** suggested an increased stability of the transient [(NMe₂Ar-BIAN)InCl₃][–]
30 complex due to the stronger electron donation from **4a** to the metal center, thus, preventing
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3 dissociation of the Ar-BIAN ligand upon reduction. This is consistent with our previous
4 observations on the voltammogram recorded for **6** bearing electron donating -OMe groups.
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8 Compound **6** also showed an electrochemically reversible reduction wave at -1.46 V, which was
9 attributed to the stronger electron donation from the corresponding -OMe substituted ligand to
10 the indium(III) center.⁵⁰ Although the assignment of each reduction and oxidation processes in
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15 **1b** to **4b** was hampered by the complex processes at the electrode surface, the redox behavior of
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18 **1b** to **4b** indicate that mild reducing agents with potentials between -1.0 V to -2.0 V can be
19 utilized to effect reduction of the In(III) complexes.⁶²
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23 In view of this, the reduction of **1b** using magnesium anthracene was attempted in THF.
24 Interestingly, based on the ^1H NMR spectra and visual observations of the reaction mixture,
25 reduction of the Ar-BIAN ligand and the indium(III) nucleus appeared to occur concurrently.
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28 Indium metal deposition was observed from the reaction mixture and the protonated reduced Ar-
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3 adopted for indium(I) complexes comprising redox innocent ligands;⁶⁷ (ii) more electron-rich
4 aryl substituents to preclude electron transfer from the indium(I) center to the Ar-BIAN ligand;
5
6 and (iii) ligands and solvents of different electronic properties to stabilize the heteroleptic
7
8 indium(I) center. Studies involving these approaches are currently undergoing.
9
10
11



32
33 **Figure 2.** UV-vis spectra for **1b** and **2b** in THF, **3b** and **5b** in DMF, and **4b** in DCM solution.
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35 All solutions were prepared, each with a concentration of 0.10 mM.
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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

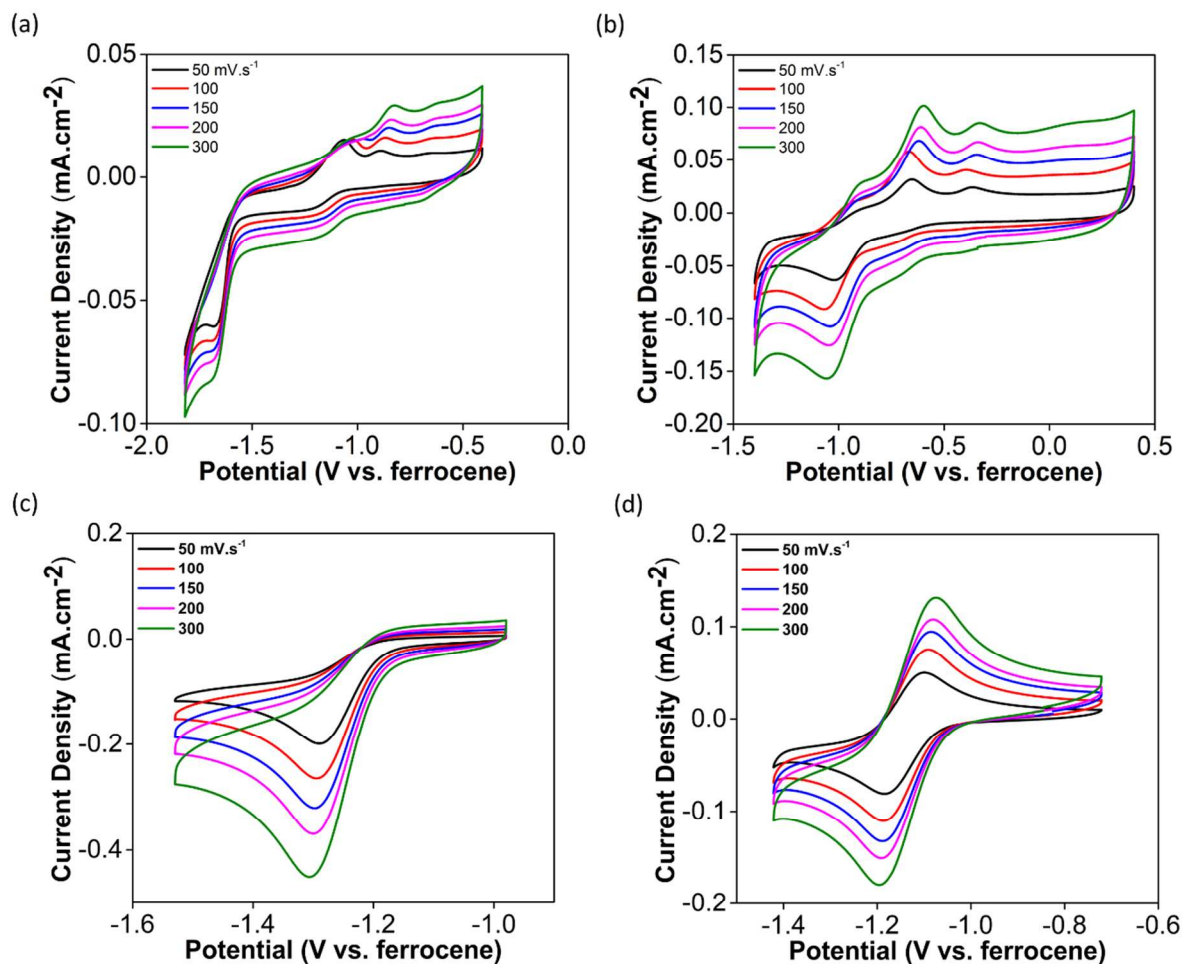
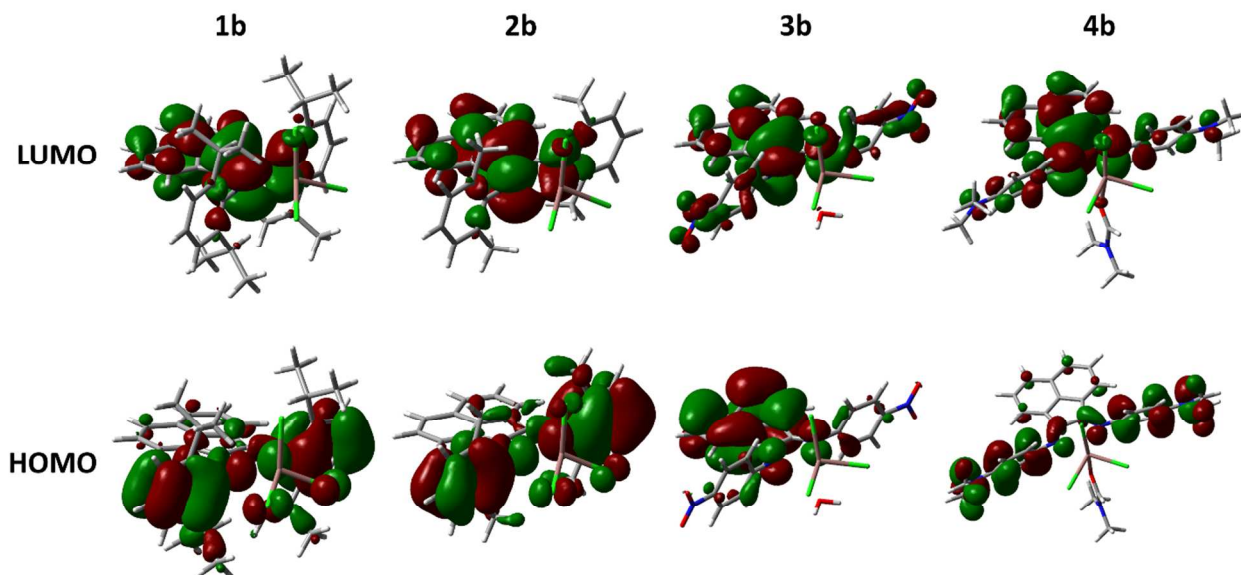


Figure 3. Cyclic voltammograms of the first reduction wave for **1b** (a) in THF, **2b** (b) in THF, **3b** (c) in DMF, and **4b** (d) in DCM solution at 298 K with 0.10 M (nBu₄N)PF₆ as the supporting electrolyte and glassy carbon (3 mm in diameter) as the working electrode. Data were collected using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

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

1
2
3 functional B3LYP/6-31+G*, using the pseudo potential LANL2DZ basis set for the indium and
4 chlorine atoms. A larger basis set 6-31++G* was used for our previously reported complexes **6**
5 and **7**, with almost identical outcomes as the ones obtained from the basis set 6-31+G*. Hence,
6 all geometry optimizations were carried out with the smaller 6-31+G* basis set in this article
7 since it would be computationally cheaper. The optimized ground state structures for all
8 complexes agreed closely with our X-ray crystallographic studies. Each optimized structure of
9 **1b** and **2b** displays a plane of symmetry bisecting the acenaphthene and indium metal center.
10 The frontier orbitals illustrating the electron density distribution for **1b** to **4b** are shown in Fig. 4.
11 For **1b**, **2b**, and **4b**, the HOMO is mostly distributed on the di(arylimine) part of the Ar-BIAN
12 ligand, while the LUMO is mainly localized on the acenaphthene moiety. However, for **3b**, the
13 HOMO is localized on the acenaphthene bay region, whereas the LUMO has distributed
14 contributions throughout the entire ligand. This intriguing reversal in orbital density when
15 strongly electron-withdrawing groups are installed on the di(arylimine) motif is consistent with
16 previous DFT calculations performed on a series of Ar-BIAN ligand by Zysman-Colman and
17 coworkers.¹⁴ From the TD-DFT analysis, the absorption maxima in **1b** and **2b** ($\lambda_{\text{max}} = 320$ nm)
18 are mainly attributed to electronic transitions from the HOMO-3 \rightarrow LUMO+1, while for **3b** (λ_{max}
19 = 318 nm), it corresponds largely to a combination of the HOMO \rightarrow LUMO+3, HOMO-1 \rightarrow
20 LUMO+2, and HOMO-8 \rightarrow LUMO transition (SI, Tables S32-S34). In the case of **4b**, the
21 calculated predominant contribution to the lower energy absorption maximum ($\lambda_{\text{max}} = 630$ nm)
22 corresponds exclusively to the HOMO \rightarrow LUMO transition, whereas the higher energy UV
23 absorption band ($\lambda_{\text{max}} = 267$ nm) consists of a combination of contributions from HOMO-
24 14 \rightarrow LUMO, HOMO-15 \rightarrow LUMO, and HOMO \rightarrow LUMO+7 transitions (SI, Table S35).
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25 **Figure 4.** Electron density distributions of the frontier orbitals for **1b** to **4b**.

26 27 28 CONCLUSIONS

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30 We have conducted a comprehensive investigation on the synthesis, absorption, and
31 electrochemical properties of a series of five indium(III) complexes bearing redox non-innocent
32 Ar-BIAN ligands. All the complexes within this study absorb light over wavelengths ranging
33 from 380 – 800 nm, with **4b** absorbing furthest to the red region, which can be attributed to the
34 small HOMO-LUMO gap due to the -NMe₂ substituent. On the other hand, the absorption
35 spectrum of **3b** revealed a single intense band at 320 nm resulting from enlarged frontier orbital
36 energy gaps arising from the electron withdrawing -NO₂ group. The CVs showed irreversible
37 reduction waves ranging from -1.2 to -1.9 V for compounds **1b** – **3b**, whereas this reduction was
38 observed to be chemically reversible for compound **4b** and our previously reported complex **6**.
39 Although disproportionation and ligand reduction were observed during our attempted reduction
40 of **1b** and **6**, we ascribe it to the non-innocent behavior of the Ar-BIAN ligand, which can
41 accommodate the extra electrons more readily than the In metal center. Future work will involve
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3 modifying both the steric and electronic properties of the Ar-BIAN ligands, as well as using
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5 different counter anions and ligands in heteroleptic systems to prevent electron transfer from the
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7 metal to the Ar-BIAN ligand.
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10 11 **EXPERIMENTAL DETAILS**

12 13 14 **General procedures**

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17 All reactions with InCl_3 and the recrystallization of products were performed under dry and inert
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19 atmospheres by using a combination of standard Schlenk line techniques and a Vacuum
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21 Atmospheres Company N_2 glovebox. Solvents including tetrahydrofuran (THF), diethyl ether
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23 (Et_2O), and pentane were distilled over Na/benzophenone and degassed using freeze-pump-thaw
24
25 cycles prior to use. Anhydrous acetonitrile (ACN) was collected from a PURE SOLV MD-5
26
27 solvent purification system and stored in a glovebox. Anhydrous 1, 2-dimethoxyethane (DME)
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29 and dichloromethane (DCM) were distilled over calcium hydride (CaH_2) and stored in a
30
31 glovebox. Anhydrous N,N-Dimethylformamide (DMF) in a Sure-Seal bottle was purchased from
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33 Sigma-Aldrich and used as received. Deuterated chloroform (CDCl_3) and acetonitrile (CD_3CN)
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35 were distilled over CaH_2 and stored over 4 Å molecular sieves. Deuterated acetone was distilled
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37 over potassium carbonate (K_2CO_3). All reagents were purchased from commercial sources and
38
39 were used without further purification. Synthetic procedures for **6** and **7** were reported by our
40
41 team previously.⁵⁰ The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 298 K on Bruker AV400
42
43 and BBFO 400 spectrometers. The chemical shift values are reported in parts per million (ppm)
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45 relative to TMS, using residual protonated solvents as the internal standards (^1H : $\delta = 7.26$ for
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47 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
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49 NMR data have not been reported due to the large quadrupolar moments of the nuclei, which
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3 result in broad and essentially unobservable NMR signals in the solid-state.⁶⁸⁻⁷⁰ This is especially
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5 the case due to the low symmetry of our reported complexes.
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8 9 **Other Instrumentation**

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11 High-resolution mass spectra were obtained by using a Waters Q-ToF Premier, with ESI mode.
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13 Crystallographic data were recorded on a Bruker X8 CCD diffractometer. UV-vis spectroscopic
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15 measurements were performed using a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer.
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17 Cyclic voltammetry (CV) experiments were conducted in a glovebox with N₂ atmosphere, using
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19 a Biologic SP-300 potentiostat with 1.0 mM solutions of each sample and 0.10 M of
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21 tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) as the electrolyte. Melting points were
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23 measured on an OptiMelt automated melting pointing system using sealed glass capillaries under
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25 argon and were uncorrected.
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32 **Synthesis of indium(III) complexes**

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36 **(dipp-BIAN)InCl₃ (1b)**: A solution of InCl₃ (0.025 g, 0.11 mmol) in THF (5 mL) was added to a
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38 solution of dipp-BIAN (0.056 g, 0.11 mmol) in THF (5 mL) at room temperature. (see
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40 Supporting Information, SI, for synthesis of dipp-BIAN) The resulting orange solution was
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42 stirred overnight, after which all volatiles were removed under vacuum. The resultant orange
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44 powder was recrystallized by vapor diffusion of pentane into a DME solution of the crude
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46 product and the isolated yield was 0.061 g (76%). ¹H NMR (400 MHz, CDCl₃): δ = 0.87 (d, *J* =
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48 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),
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50 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).
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52 ¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 24.4, 24.8, 29.9, 125.1, 126.2, 127.8, 129.1, 129.3, 131.1,
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54 133.2, 140.0, 140.3, 144.3, 162.7. m.p.: decomposed at 280°C HRMS (ESI+, *m/z*) calculated for
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3 C₃₆H₄₀N₂InCl₃Na [M+Na]⁺ *m/z* = 743.1194, found 743.1179. Anal. Calcd. for C₃₆H₄₀N₂InCl₃: C,
4 59.90; H, 5.59; N, 3.88. Found: C, 59.56; H, 5.43; N, 3.82.
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9 **(2,6-Me₂Ar-BIAN)InCl₃ (2b):** The procedure was identical to the one reported above for **1b**.
10 The following quantities of reagents were used: InCl₃ (0.023 g, 0.10 mmol) in THF (5 mL), 2,6-
11 Me₂Ar-BIAN (0.040 g, 0.10 mmol) in THF (5 mL). (see SI for synthesis of 2,6-Me₂Ar-BIAN)
12
13 Orange block-like crystals suitable for single crystal X-ray analysis were obtained by
14 recrystallization via vapor diffusion of pentane into a THF solution of the crude product and the
15 isolated yield was 0.026 g (41%). ¹H NMR (400 MHz, CDCl₃): δ = 2.30 (s, 12 H), 6.79 (d, *J* =
16 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
17 Hz, 2 H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 19.0, 125.8, 126.7, 128.4, 129.6 (two
18 overlapping signals), 129.9, 131.1, 133.5, 142.1, 144.6, 162.3. m.p.: decomposed at 273°C
19
20 HRMS (ESI+, *m/z*) calculated for C₂₈H₂₄N₂InCl₃Na [M+Na]⁺ *m/z* = 630.9942, found 630.9954.
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22 Anal. Calcd. for C₂₈H₂₄N₂InCl₃·THF·H₂O: C, 54.92; H, 4.90; N, 4.00. Found: C, 55.16; H, 4.93;
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24 N, 4.26.
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38 **(*p*-NO₂Ar-BIAN)InCl₃ (3b):** The procedure was similar to the one reported above for complex
39 **1b** except that this reaction was carried out under reflux conditions overnight. The following
40 quantities of compounds were used: InCl₃ (0.044 g, 0.20 mmol) and *p*-NO₂Ar-BIAN (0.084 g,
41 0.20 mmol) in THF (7 mL). (see SI for synthesis of *p*-NO₂Ar-BIAN) The resultant yellow solid
42 was purified by washing with THF and the isolated yield was 0.083 g (64%). The purity of the
43 product was confirmed by elemental analysis. Yellow block-like crystals suitable for single
44 crystal X-ray analysis were obtained by recrystallization from an ACN solution of the crude
45 product. ¹H 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
46 (d, *J* = 8.4 Hz, 2 H), 8.55-8.58 (m, 4 H). The ¹³C{¹H} NMR could not be obtained due to the
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3 poor solubility of **3b** in most of the available deuterated solvents. m.p.: decomposed after 320°C
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5 HRMS (ESI+, m/z) calculated for $C_{24}H_{14}Cl_3InN_4O_4Na$ $[M+Na]^+$ $m/z = 664.9017$, found
6
7 664.9005. 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;
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9 H, 3.45; N, 8.15.
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14 **(*p*-NMe₂Ar-BIAN)InCl₃ (4b)**: The procedure was identical to the one reported above for **1b**.

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16 The following quantities of reagents were used: InCl₃ (0.066 g, 0.30 mmol) in THF (5 mL), *p*-
17
18 NMe₂Ar-BIAN (0.130 g, 0.30 mmol) in THF (5 mL). (see SI for synthesis of *p*-NMe₂Ar-BIAN)
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20 The purple solution was stirred overnight, after which all volatiles were removed under vacuum.

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22 The resultant deep blue solid was washed with Et₂O. Purple needle-like crystals suitable for
23
24 single crystal X-ray analysis were obtained from recrystallization by vapor diffusion of Et₂O into
25
26 a DMF solution of the crude product and the isolated yield was 0.13 g (68%). ¹H NMR (400
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28 MHz, CD₂Cl₂, 25 °C, *fac*-isomer): $\delta = 3.09$ (s, broad, 12 H), 6.88 (d, $J = 9.2$, 2 H), 7.04-7.06 (m,
29
30 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). ¹³C{¹H} NMR (100
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32 MHz, CD₂Cl₂): $\delta = 40.6$, 40.7, 112.5, 123.0 (broad, may have peaks overlapping), 124.3, 126.1
33
34 (broad, may have peaks overlapping), 127.2, 128.8, 129.1, 131.3 (two peaks), 131.7, 132.8
35
36 (broad, may have peaks overlapping), 133.5, 143.8, 144.1, 150.9, 151.3 (broad, may have peaks
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38 overlapping), 157.7. m.p. 198-202°C HRMS (ESI+, m/z) calculated for $C_{31}H_{33}N_5InCl_3Na$
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40 $[M+Na]^+$ $m/z = 734.0687$, found 734.0652. Anal. Calcd. for $C_{31}H_{33}N_5OInCl_3 \cdot H_2O$: C, 50.95; H,
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42 4.83; N, 9.58. Found: C, 50.90; H, 4.90; N, 9.32.
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50 **(*p*-MeOAr-BIAN)InCl₃•DMF (5b)**:⁵⁰ The synthetic procedure was reported in a recent
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52 publication by our team and it has been included here for completeness. Recrystallization by
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54 vapor diffusion of Et₂O into a DMF solution of the red solid resulted in samples suitable for
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56 single crystal X-ray analysis. ¹H NMR (400 MHz, CD₃CN, *fac*-isomer): $\delta = 3.92$ (s, 6 H), 7.16-
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3 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). $^{13}\text{C}\{^1\text{H}\}$ 3.33
4
5 NMR (100 MHz, DMF- d_7): $\delta = 56.4, 114.4, 115.8, 116.0, 119.9, 120.4$ (broad overlapping
6
7 peaks), 122.8, 124.3 (broad overlapping peaks), 124.6, 127.2 (broad overlapping peaks), 129.0
8
9 (broad overlapping peaks), 130.1, 130.3, 133.5, 138.7, 158.1, 160.6. HRMS (ESI+, m/z)
10
11 calculated for $\text{C}_{29}\text{H}_{27}\text{Cl}_3\text{InN}_3\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ $m/z = 708.0054$, found 708.0081. Anal. Calcd. for
12
13 $\text{C}_{29}\text{H}_{27}\text{N}_3\text{O}_3\text{InCl}_3 \cdot \text{H}_2\text{O}$: C, 49.43; H, 4.15; N, 5.96. Found: C, 49.84; H, 4.55; N, 6.12.
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18 **Reduction of $[(p\text{-MeOAr-BIAN})_2\text{InCl}_2]^+[\text{InCl}_4]^-$ (6):** A THF solution (5 mL) of CoCp_2 was
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20 added dropwise to a THF suspension (5 mL) of **6** at room temperature. The resulting brown
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22 suspension was stirred for 2 h, after which all volatiles were removed under vacuum. The crude
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24 purple solid was washed with Et_2O and the purple filtrate was filtered and concentrated. The ^1H
25
26 NMR experiments were conducted on the resultant purple solid. ^1H NMR (400 MHz, C_6D_6):
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28 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
29
30 C_6D_6), 7.43 (d, $J = 8.0$ Hz, 2 H).
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36 Theoretical basis

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39 DFT calculations were used to evaluate both the geometries and energies of the different indium
40
41 complexes possessing one or two coordinated Ar-BIAN ligands. The initial energy and geometry
42
43 optimization was carried out at the B3LYP⁷¹⁻⁷³ level with the 6-31+G* basis set for non-metal
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45 atoms⁷⁴, together with the pseudo potential LANL2DZ⁷⁵ for the In and Cl atoms. The agreement
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47 between the experimentally determined and the computed structures supports the method used.
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50 Frequency calculations were carried out at this level to confirm that a minimum had been
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52 achieved. To account for solvent effects, a reaction field calculation with radii and non-
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3 electrostatic terms and the SMD solvation model was used.⁷⁶ All the TD-DFT calculations were
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5 carried out using the Gaussian 09 program package.^{71-73, 77}
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28 29 **ASSOCIATED CONTENT**

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33 **Supporting Information.** General procedures, experimental details, photophysical and
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35 electrochemical characterization protocols, ¹H and ¹³C NMR spectra, crystallographic data
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37 (CCDC 1535077-1535081) and computational details. This material is available free of charge
38
39 via the Internet at <http://pubs.acs.org> with DOI: 10.1021/acs.inorgchem.XXXXXXX.
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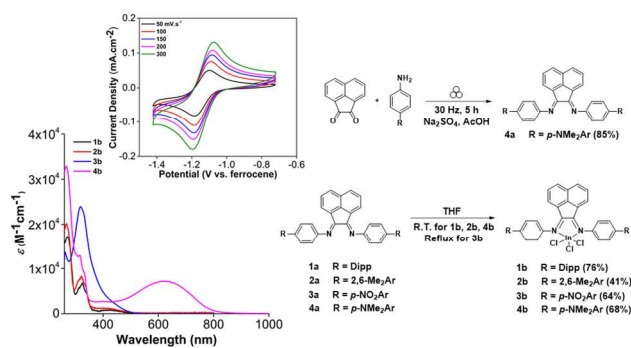
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TOC graphic “For Table of Contents Only”

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.



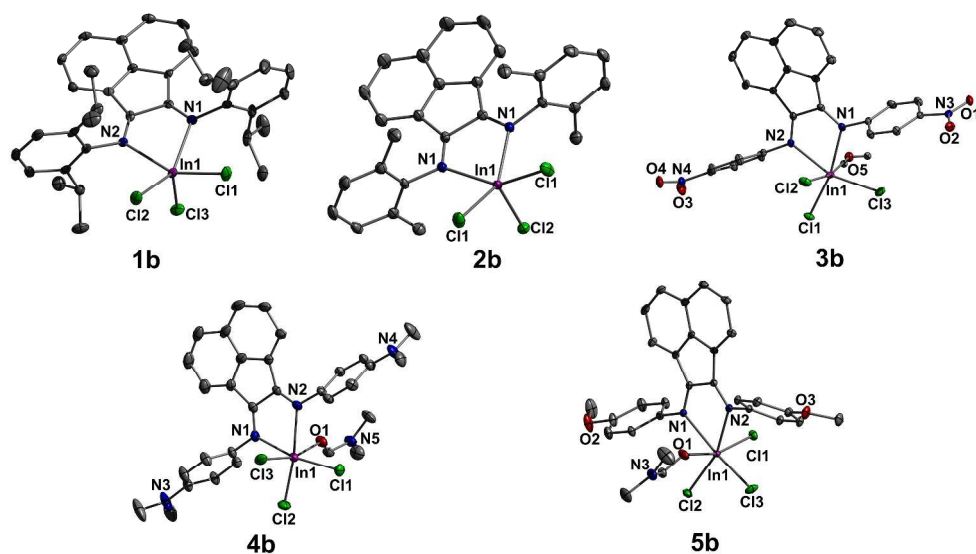


Figure 1. Selected bond lengths (\AA) and angles ($^\circ$) of complexes (1b) In1-N1 2.342(5), In1-N2 2.339(5), In1-Cl1 2.3835(16), In1-Cl2 2.3800(17), In1-Cl3 2.3643(17); (2b) In1-N1 2.3196(15), In1-Cl1 2.3897(5), In1-Cl2 2.3769(7); (3b) In1-N1 2.3230(14), In1-N2 2.3114(14), In1-Cl1 2.4013(4), In1-Cl2 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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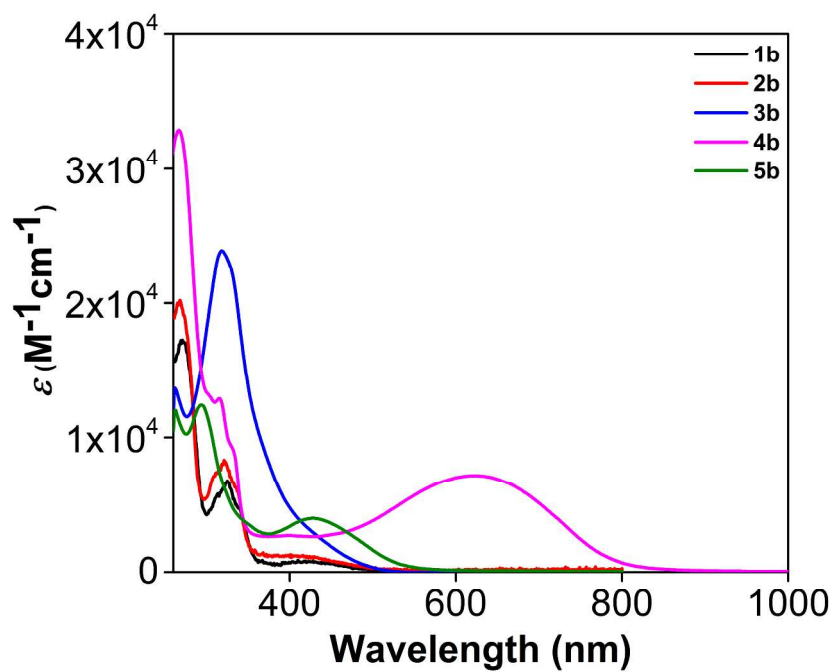


Figure 2. UV-vis spectra for 1b and 2b in THF, 3b and 5b in DMF, and 4b in DCM solution. All solutions were prepared, each with a concentration of 0.10 mM.

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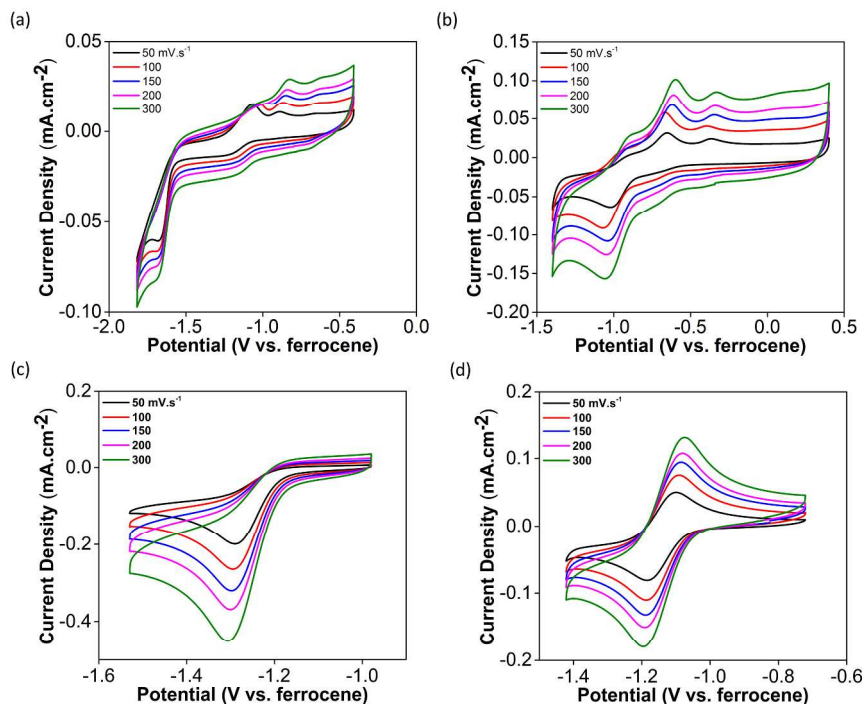
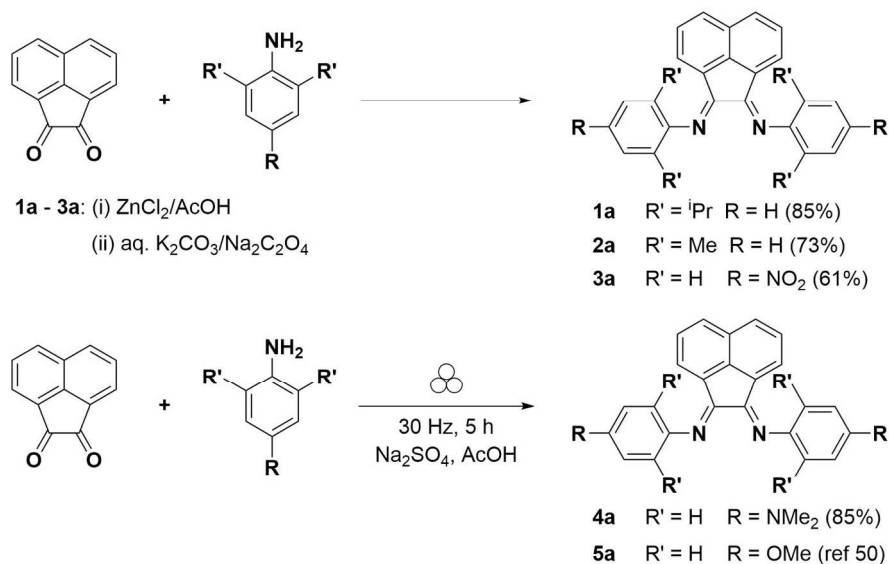


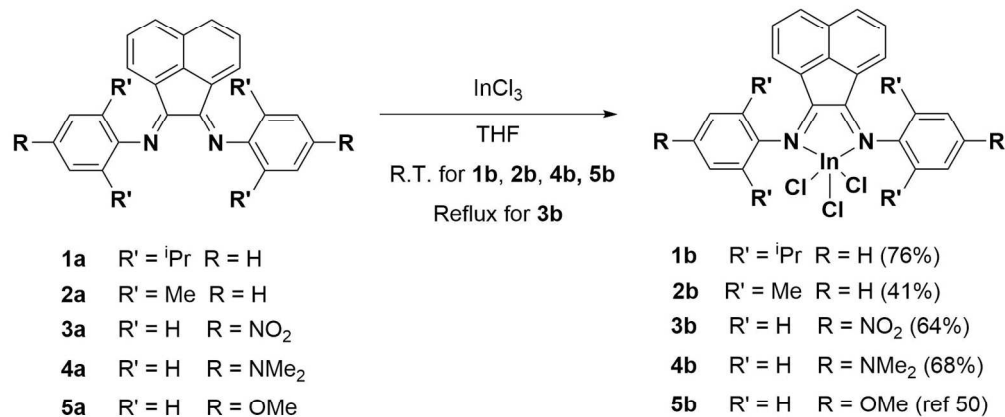
Figure 3. Cyclic voltammograms of the first reduction wave for 1b (a) in THF, 2b (b) in THF, 3b (c) in DMF, and 4b (d) in DCM solution at 298 K with 0.10 M (nBu₄N)PF₆ as the supporting electrolyte and glassy carbon (3 mm in diameter) as the working electrode. Data were collected using scan rates ranging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

254x190mm (300 x 300 DPI)



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

338x190mm (300 x 300 DPI)



Scheme 2 Synthetic route to 1b – 5b.

338x190mm (300 x 300 DPI)