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## Bay-Region Functionalisation of Ar-BIAN Ligands and Their Use Within Highly Absorptive Cationic Iridium(III) Dyes

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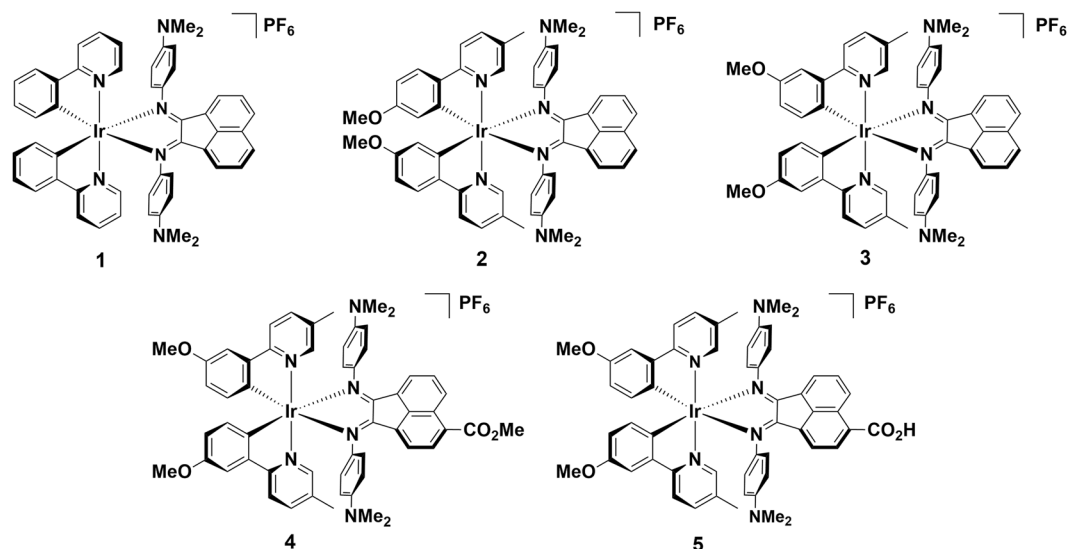
We report the synthesis, UV-vis absorption, electrochemical characterisation, and DFT studies of five panchromatic, heteroleptic iridium complexes (four of which are new) supported by Ar-BIAN ligands. In particular, the synthesis of an ester-functionalised Ar-BIAN ligand was carried out by a mechanochemical milling approach, which was advantageous over conventional metal templating solution methods in terms of reaction time and product purity. The introduction of ester and carboxylate functionalities at the bay region of the acenaphthene motif increases each ligand's  $\pi$ -accepting capacity and imparts grafting capabilities to the iridium complexes. These complexes have absorption profiles that surpass the renowned N3 dye [Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>] (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine), making them of interest for solar-energy-harvesting applications.

There is growing recognition of the need for alternative sources of energy to reduce our reliance on fossil fuels and overcome the challenges of global climate change and environmental pollution. Solar energy is one of the sustainable alternatives, and several promising approaches to use sunlight include the generation of electricity with photovoltaics, the production of solar fuels and chemicals by artificial photosynthesis, and the storage of solar thermal energy<sup>1</sup>. One of the established technologies that can be exploited for both photovoltaics and artificial photosynthesis is the dye-sensitised solar cell (DSSC)<sup>2</sup>, which has lately been adapted for the production of solar chemicals in a dye-sensitised photoelectrosynthesis cell (DSPEC)<sup>3-6</sup>. The workhorse behind both the DSSCs and the DSPECs are the photosensitisers that absorb UV to NIR radiation<sup>2-6</sup>, but notably, the dyes predominantly comprise heteroleptic ruthenium complexes (e.g. the celebrated N3 dye) or complicated porphyrin systems<sup>7,8</sup>. On the contrary, iridium-based photosensitisers have received greater attention in the nascent field of photoredox catalysis for organic syntheses<sup>9-13</sup>. Iridium complexes have potential benefits of higher thermal and chemical stability, similar quantum yields, and longer-lived excited states in comparison to ruthenium compounds<sup>14</sup>, and iridium systems have been successfully deployed in numerous light harvesting and emitting applications<sup>15-19</sup>. Despite this, there has been a dearth of reports on iridium-based photosensitisers in DSSCs or DSPECs<sup>14</sup>.

Our team has sought to expand the library of potential candidates for light harvesting by developing iridium and other metal complexes composed of bis(arylimino)acenaphthene (Ar-BIAN) ligands that are highly modular and can be readily synthesised from commercially available reagents<sup>20-24</sup>. The Ar-BIANs are known to be versatile  $\pi$ -acceptors and have been employed for hydroamination and hydrogenation catalysis with iridium complexes<sup>25-27</sup>. We surmised that the Ar-BIAN ligand can be functionalised with an electron-withdrawing anchoring functionality such as a carboxylate, with the dual function of facilitating grafting on the surface of metal oxides, and also enhancing the absorption profile. Herein, we describe the synthesis of the first Ar-BIAN

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**Figure 1.** Complexes investigated in this study.

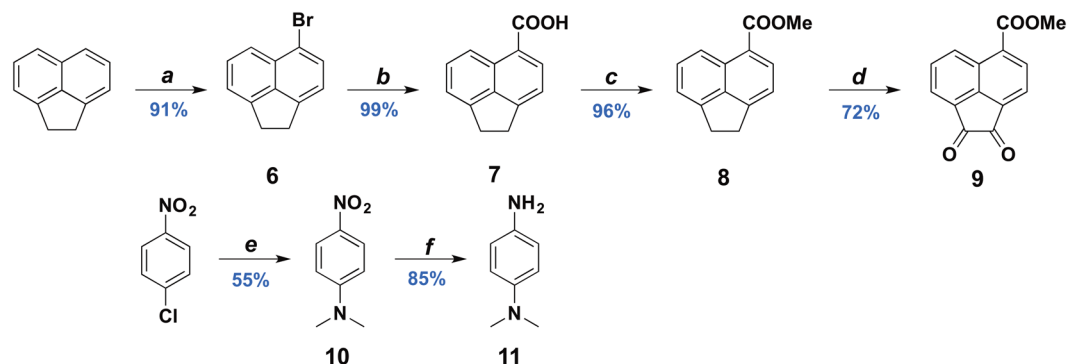
ligand possessing methyl carboxylate and carboxylic acid substituents in the bay region of the acenaphthene motif *via* a mechanochemical milling approach, in which reactions are induced by mechanical energy through ball milling and grinding<sup>28</sup>.

Although solution-based methods have traditionally been utilised for chemical synthesis by default, there has been increasing interest in recent years towards mechanochemical synthesis, partly because it has been shown to reduce reaction times and can sometimes provide almost quantitative yields<sup>29</sup>. A specific mechanochemical technique is ball milling, in which reaction vessels are oscillated from side-to-side<sup>30</sup>. This motion creates impact between the ball-bearing inside the reaction vessel, the chemical contents, and the walls of the vessel, providing energy input to drive chemical reactions. The speed and milling time, together with the size of the ball bearing in the reaction vessel are adjustable and can be systematically varied<sup>30</sup>. Mechanochemical synthesis through ball milling is a more eco-friendly, essentially solvent-free approach that has been exceptionally effective to access metastable compounds and materials that may react with coordinating solvents<sup>31</sup>. We present optical absorption spectroscopy, electrochemical measurements, and density functional theory (DFT) calculations of a series of five complexes (Fig. 1) to highlight how we have achieved panchromatic light absorption with modest effects on the electrochemical potentials, indicating that the carboxylate on the Ar-BIAN ligand can potentially be employed in DSSCs and DSPECs.

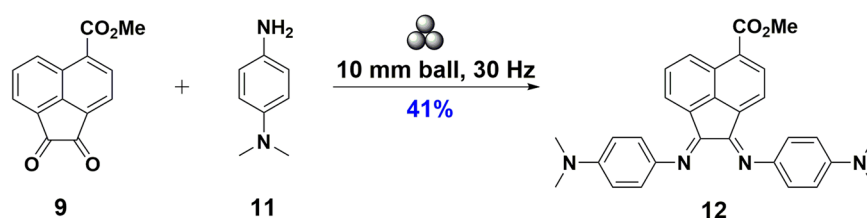
## Results and Discussion

The synthesis of 5-carboxymethylacenaphthoquinone, **9**, and *N,N*-dimethyl-4-phenylenediamine, **11**, is outlined in Fig. 2. Although compounds **6**, **10**, and **11** are commercially available, we elected to synthesise them from much more affordable precursors. Acenaphthene was regioselectively monobrominated at the 5-position using *N*-bromosuccinimide in acetonitrile (MeCN)<sup>32</sup>. The vital carboxymethyl group was installed in two steps. Lithiation of **6** and quenching with dry ice<sup>33</sup> yielded **7**, following which **7** was esterified using thionyl chloride and methanol to afford **8** in excellent yield<sup>34</sup>. Oxidation of **8** with chromium trioxide in acetic anhydride following the procedure of Pei and co-workers<sup>35</sup> resulted in the formation of an inseparable mixture of dione **9** and a second similarly symmetric product, putatively identified as the enediol by <sup>1</sup>H NMR spectroscopy. Initially, we attempted to prepare ligand **12** *via* solution methods through a ZnCl<sub>2</sub> templated condensation between **9** and **11**<sup>36</sup>, the latter of which was obtained in two steps from 4-chloronitrobenzene *via* nucleophilic aromatic substitution with DMF<sup>37</sup>, followed by reduction of the nitro group to the corresponding amine<sup>38</sup>. This templating method with ZnCl<sub>2</sub> was deemed necessary because acid-catalysed condensation reactions do not work well with sterically hindered ketones and amines. Furthermore, Cenini *et al.* showed that the driving force for this double condensation is the precipitation of the metal Ar-BIAN complex. In cases where the final metal complex did not precipitate out, the product was formed in only minute amounts<sup>39</sup>. However, in the present case, attempts at removal of the Zn salts often led to hydrolysis, hindering purification of the ligand. Instead, ligand **12** was successfully obtained by mechanochemical synthesis through an acetic acid-catalysed condensation between **9** and **11** (Fig. 3). Mechanochemical synthesis through ball milling has been found to be remarkably effective for the solid-state synthesis of both organic and inorganic molecules, including an indium Ar-BIAN complex from our team, and has been especially advantageous for the facile synthesis and purification of **12** here<sup>23</sup>.

In parallel, 2-(3'-anisyl)-5-methylpyridine (3MeO-5Meppy) and 2-(4'-anisyl)-5-methylpyridine (4MeO-5Meppy) were obtained in 47 and 95% yield, respectively, through the Suzuki coupling of 2-bromo-5-methylpyridine and the corresponding arylboronic acids<sup>36,40</sup>. The corresponding chloro-bridged iridium(III) dimers were then isolated in 68 and 71% yield, respectively, following the procedure of Watts and co-workers<sup>41</sup>. We had previously



**Figure 2.** Synthesis of 5-carboxymethylacenaphthoquinone, **9**, and *N,N*-dimethyl-4-phenylenediamine, **11**. (a) 1 equiv. NBS/MeCN, RT, 19 h; (b) i. 1.5 equiv. *n*-BuLi,  $-78^{\circ}\text{C}$  30 min; ii. CO<sub>2</sub>(s), RT; (c). 2.5 equiv. SOCl<sub>2</sub>/MeOH, reflux, 19 h; (d) i. 7.8 equiv. CrO<sub>3</sub>/Ac<sub>2</sub>O, 110 °C; ii. conc. HCl, 0 °C; (e) 10 equiv. KOH/DMF, 155 °C, 19 h; (f) 3 equiv. NaBH<sub>4</sub>, 20 mol% Cu(acac)<sub>2</sub>/1:1 v/v *i*-PrOH:EtOH, 35 °C, N<sub>2</sub>, 9 h.

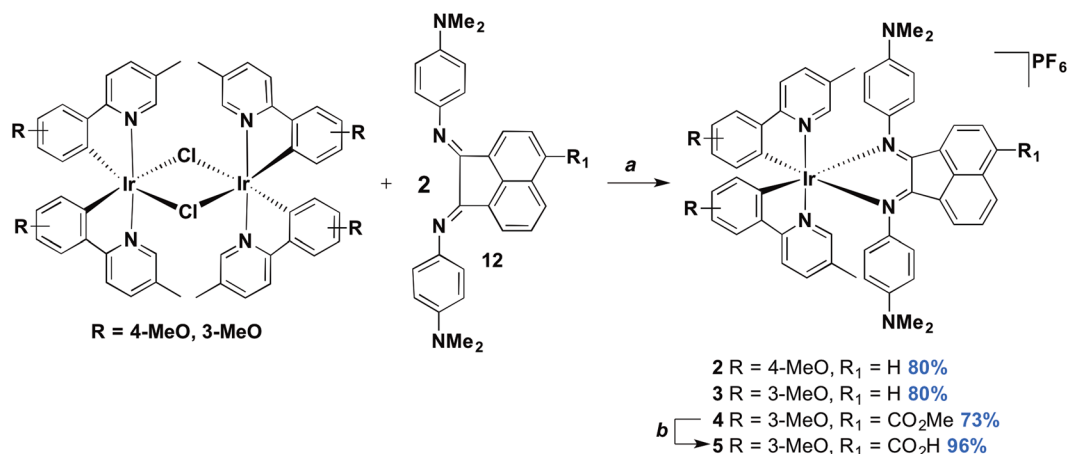


**Figure 3.** Mechanochemical synthesis of a methyl ester-modified Ar-BIAN ligand. The symbol for mechanical milling above the arrow of the equation has been proposed by Hanusa *et al.*<sup>31</sup>.

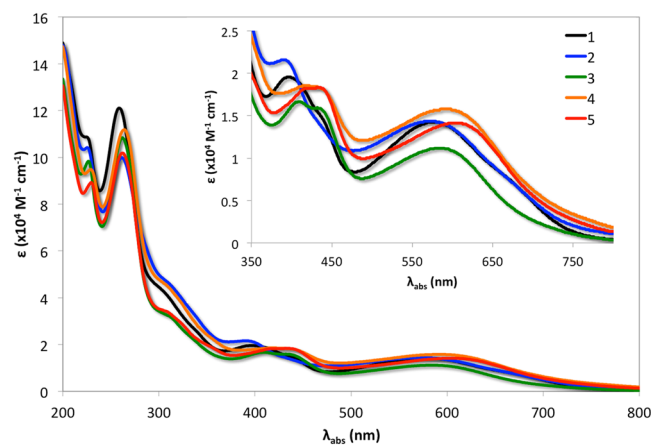
reported **1**<sup>20</sup>, a reference compound for our current manuscript, and we adopted a similar protocol to synthesise mononuclear complexes **2–4**. The new Ir complexes were prepared in good yields through cleavage of the corresponding iridium dimer, [Ir(C<sup>^</sup>N)<sub>2</sub>(μ-Cl)]<sub>2</sub>, with the corresponding Ar-BIAN ligands (Fig. 4). Saponification of the methyl ester in **4** afforded complex **5** almost quantitatively. The identity and purity of **2–5** were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, melting points, and high-resolution mass spectrometric (HRMS) analyses.

To assess the light absorption behavior among our iridium(III) complexes, the UV-vis-NIR absorption spectra were collected in acetonitrile (MeCN) solution and are illustrated in Fig. 5. Some of the significant absorption band maxima along with their corresponding molar extinction coefficients are collected in Table 1. Overlays of experimentally observed and theoretically predicted absorption data by TD-DFT are shown in Supplementary Figs S23–S27. In all of these complexes, the HOMO resides on the *N,N*-dimethylaniline part of the Ar-BIAN ligand and the LUMO resides on the acenaphthylene-1,2-dimine core of the Ar-BIAN ligand (Fig. 6). The intense bands in the UV region at ~225 nm are assigned to be spin-allowed ligand-centered (<sup>1</sup>LC) <sup>1</sup>(π-π\*) transitions<sup>37</sup>. For **1**, the band at 258 nm is an admixture of <sup>1</sup>LC, (<sup>1</sup>(π<sub>Ar-BIAN</sub>-π<sub>Ar-BIAN</sub>\*)) and singlet ligand-ligand charge transfer (<sup>1</sup>LLCT) (Ar-BIAN(π) to ppy(π\*)) transitions (Supplementary Table S1). For complexes **2–5**, the bands at ~260 nm consist primarily of <sup>1</sup>LLCT (Ar-BIAN(π) to ppy(π\*)) or <sup>1</sup>LC (<sup>1</sup>(π<sub>ppy</sub>-π<sub>ppy</sub>\*)) for **3–5**, with minor contributions from singlet metal-to-ligand charge-transfer (<sup>1</sup>MLCT) (Ir(dπ) to ppy(π\*)) for **2–5** (Supplementary Tables S1–S5). Similarly, the bands at ~310 nm of **1–5** also possess varying contributions of <sup>1</sup>LC, <sup>1</sup>LLCT, and <sup>1</sup>MLCT transitions (Supplementary Tables S1–S5). Despite the structural variation on both sets of ligands in **1–5**, the energies of these higher-energy absorption bands differ very little across the series.

Inspection of the lower energy region of the spectrum reveals a more notable structure-property relationship. The absorption bands in **1** and **2** between 390–396 and 570–576 nm are shifted bathochromically in **3–5** to 409–427 nm and 585–604 nm, respectively. For **1–3**, the set of bands at 390–409 nm are composed of an admixture of <sup>1</sup>LLCT (ppy(π) to Ar-BIAN(π\*)) and <sup>1</sup>MLCT (Ir(dπ) to Ar-BIAN(π\*)) transitions, whereas bands in **4** and **5** at 416 nm and 427 nm, respectively, are described primarily by <sup>1</sup>LC (ppy(π) to ppy(π\*)) transitions with minor contributions from <sup>1</sup>MLCT (Ir(dπ) to ppy(π\*)) transitions (Supplementary Tables S1–S5). The magnitude of the red-shift for the absorption bands around 590 nm increases from **3** to **5**, while the bands centered around 400 nm are less sensitive to the functionalisation in the bay region of the acenaphthene core. The bands at 570–576 nm in **1** and **2** are principally <sup>1</sup>LLCT (ppy(π) to Ar-BIAN(π\*)) in nature with minor contribution from <sup>1</sup>MLCT (Ir(dπ) to Ar-BIAN(π\*)) (Supplementary Tables S1 and S2). For **3**, the band at 585 nm is an admixture of transitions, primarily consisting of <sup>1</sup>LC (Ar-BIAN/ppy(π) to Ar-BIAN/ppy(π\*)) with minor <sup>1</sup>LLCT (Ar-BIAN(π) to ppy(π\*)) contributions (Supplementary Table S3). On the other hand, notably, the bands at 590 nm and 604 nm in **4** and **5**, respectively, are composed exclusively of intra-ligand charge-transfer transitions (<sup>1</sup>ILCT) within the Ar-BIAN moiety (Supplementary Tables S4 and S5). Moreover, as the conjugative framework of the ancillary



**Figure 4.** Synthesis of iridium(III) complexes 2–5. (a) i. DCM, 50 °C, 19 h; ii. NH<sub>4</sub>PF<sub>6</sub> (aq); (b) 2.7 equiv. NaOH/1:1 MeCN:H<sub>2</sub>O v/v, 85 °C, 22 h.



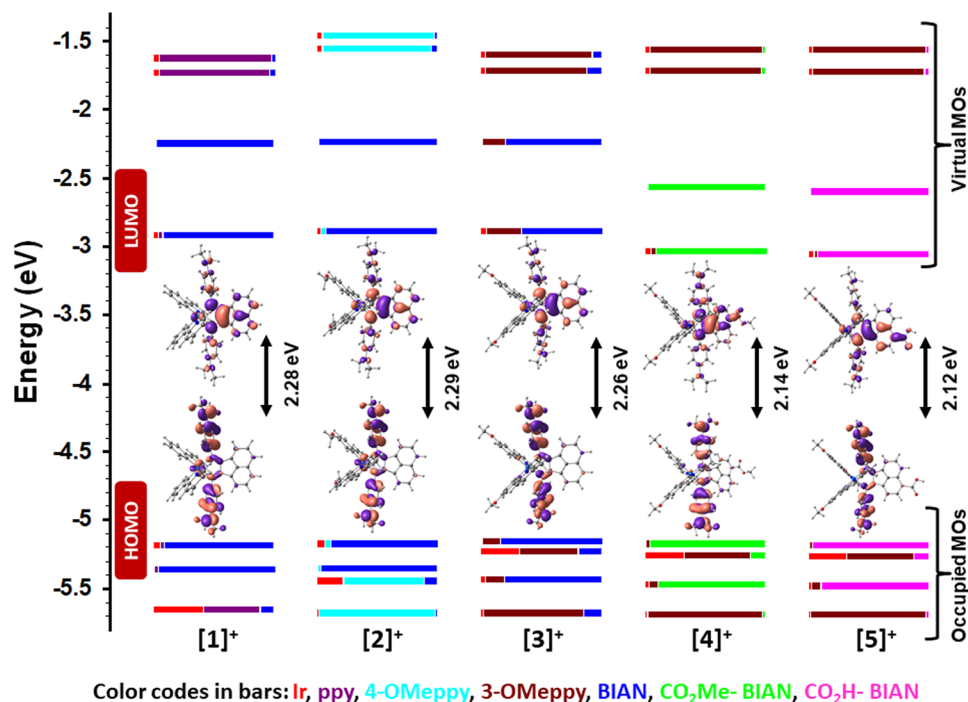
**Figure 5.** Electronic absorption spectra of 1–5 recorded in MeCN at 298 K. Inset: Expanded UV-vis-NIR absorption spectra from 350–800 nm.

Complex	$\lambda_{\text{abs}} / \text{nm}$ ( $\epsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) <sup>a</sup>
<b>1</b>	224 (10.9); 258 (12.1); 310 (sh, <sup>b</sup> 4.02); 396 (1.95); 576 (1.42); 675 (sh, <sup>b</sup> 0.71)
<b>2</b>	225 (10.4); 261 (9.99); 310 (sh, <sup>b</sup> 4.62); 390 (2.15); 570 (1.43); 665 (sh, <sup>b</sup> 0.78)
<b>3</b>	227 (9.82); 262 (10.8); 312 (sh, <sup>b</sup> 3.18); 409 (1.66); 432 (1.59); 585 (1.11)
<b>4</b>	229 (9.48); 264 (11.2); 309 (sh, <sup>b</sup> 4.48); 416 (1.85); 590 (1.57)
<b>5</b>	229 (8.91); 262 (10.2); 310 (sh, <sup>b</sup> 3.37); 427 (1.82); 604 (1.41)

**Table 1.** Spectroscopic data for 1–5. <sup>a</sup>Absorption spectra recorded in aerated MeCN at 298 K. Absorbance values were collected over a concentration range of  $8.78 \times 10^{-2}$  to  $3.51 \times 10^1 \mu\text{M}$ , and the molar extinction coefficients ( $\epsilon$ ) were determined by assuming the complexes obeyed the Beer-Lambert law. <sup>b</sup>Shoulder.

ligand is expanded with the incorporation of the carboxy moiety in 4 and 5, the molar extinction coefficients of the charge-transfer (CT) bands also increase.

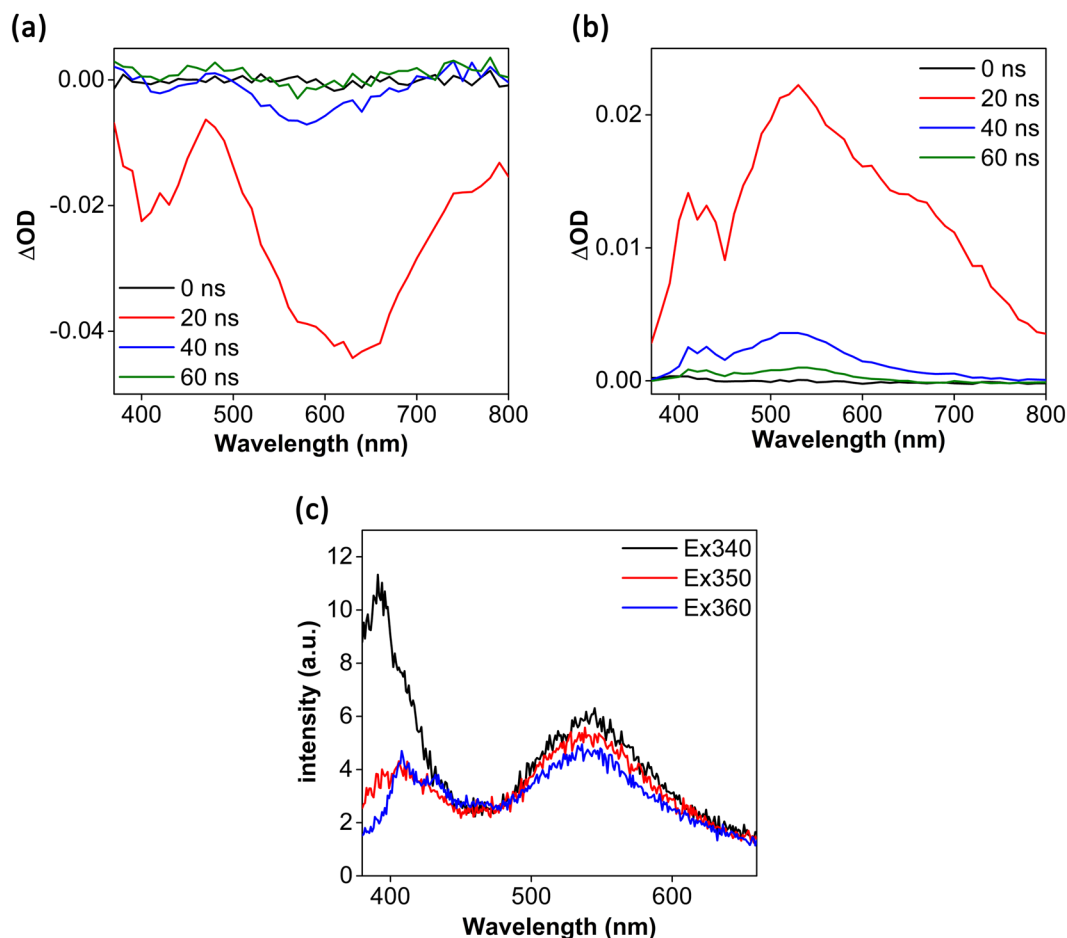
The absorption bands at  $\lambda_{\text{abs}} > 600 \text{ nm}$  in 1 and 2 are principally <sup>1</sup>ILCT and <sup>1</sup>LLCT in character, respectively (Ar-BIAN( $\pi$ ) to Ar-BIAN( $\pi^*$ ) for 1 and ppy( $\pi$ ) to Ar-BIAN( $\pi^*$ ) for 2). Although no distinct bands at  $\lambda_{\text{abs}} > 600 \text{ nm}$  could be observed for 3–5, spin-forbidden <sup>3</sup>CT transitions at 752–783 nm with very low molar absorptivity are predicted by TD-DFT. Quantification of the light-harvesting capacities of 1–5 and comparison to that of the benchmark dye N3, [Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>] consisted of an analysis of the integrated product of their absorption spectra with the AM 1.5 solar irradiance spectrum over the range of 400–800 nm (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine). Complexes 1, 3, and 5 absorb 1.56, 1.47, and 2.19 times more light over this spectral range compared to N3. The light harvesting capacity of 5 is in fact even larger since its absorption profile extends beyond 800 nm.



**Figure 6.** Calculated frontier Kohn-Sham MOs of 1–5. DFT calculations were performed with the B3LYP/SBKJC-VDZ basis set for Ir(III) and 6–31 G\*\* for C, H, N, and O, using a CPCM (MeCN) solvent model. The orbitals are isocontoured at 0.02.

In order to examine the time-resolved photophysical properties of the Ir complexes, steady-state photoluminescence (PL) spectra were first recorded for **4** (in DCM) and **5** (in MeCN since it is insoluble in DCM). For compound **4**, weak emission was observed at 540 and 410 nm when the sample was excited at 420 and 340 nm, respectively (Fig. 7). A similar emission profile was also observed when **5** was irradiated at the same wavelengths (Supplementary Fig. S28). We propose that the two emission bands may arise from mixed MLCT/ILCT transitions due to the two different ligand motifs. Both the C<sup>^</sup>N and Ar-BIAN ligands are  $\pi$ -acceptors, although the  $\pi^*$  orbitals of the Ar-BIAN ligand are lower in energy due to more extensive conjugation. Thus, we expect that there could be MLCT/ILCT/LLCT excited states arising from promotion of the Ir  $d$  electrons to the two distinct ligand  $\pi^*$  orbitals, resulting in radiative recombination from the Ar-BIAN ligand back to Ir, between the C<sup>^</sup>N and Ar-BIAN ligands, and within the Ar-BIAN ligand at a lower energy. The spin density distribution obtained from unrestricted DFT calculations are predominantly distributed within the Ar-BIAN ligand, with minor contributions from the Ir center (Fig. 8). The overall photoluminescence quantum yield,  $\phi_{\text{PL}}$ , for **4** was estimated to be 0.03% in DCM, using the comparative method described by Williams *et al.*<sup>42</sup>

To obtain additional insights into the excited state characteristics of these Ir complexes, nanosecond transient absorption and emission spectroscopic measurements were conducted (Fig. 7). In each time resolved optical spectroscopic experiment, the sample was probed by a broadband xenon lamp beam before and after 5–8 ns pulses. In the transient absorption spectra, the detected intensity of the transmitted signal is presented as  $\Delta OD$ , which is the logarithm of the ratio of the light intensity from the probe beam after laser excitation to the intensity before laser excitation. Hence, a positive  $\Delta OD$  refers to increased absorption while a negative  $\Delta OD$  refers to reduced absorption/emission of the excited state relative to the ground state. The transient emission spectra show two broad emission bands with maxima at 410 nm and 530 nm when irradiated by a 355 nm laser pulse, matching the spectral profile derived from the steady-state PL experiments. On the other hand, the transient absorption spectra reveal two bands with negative  $\Delta OD$  peaked at 410 and 630 nm, which results from a superposition of both the excited state emission and the ground state bleach, since a fraction of the molecules has been promoted to the excited state by the laser pulse. We attempted to estimate the excited  $[\text{Ir}]^{+*}$  lifetime at 520 nm (and other wavelengths), but the lifetime turned out to be shorter than the time-resolution of our instrument (Supplementary Fig. S29). Nevertheless, the steady-state and time-resolved spectroscopic studies confirmed that both **4** and **5** exhibit weak PL with time-scales consistent with fluorescence. There is overlap between the PL and the absorption spectra for both **4** and **5**, concurring with our previous assignment that the spin-allowed fluorescence arises from the  $^1\text{ILCT}/^1\text{MLCT}/^1\text{LLCT}$  absorptions at higher energy, whereas the lowest energy absorption bands are due to spin-forbidden CT transitions ( $\lambda_{\text{abs}} > 600$  nm). As reported by Tkachenko *et al.*, the MLCT excited state for complexes with Ar-BIAN ligands decays to an intra-molecular Ar-BIAN triplet state, which typically decays back to the ground state on the order of picoseconds<sup>43</sup>. This is likely due to the substantial spatial overlap of the HOMO and LUMO at the bis(arylimine) part of the ligand, which facilitates ultrafast recombination. Presumably, the  $\pi$ -accepting orbitals become more localised on the acenaphthene bay region, which provides better spatial separation of the electron from Ir after



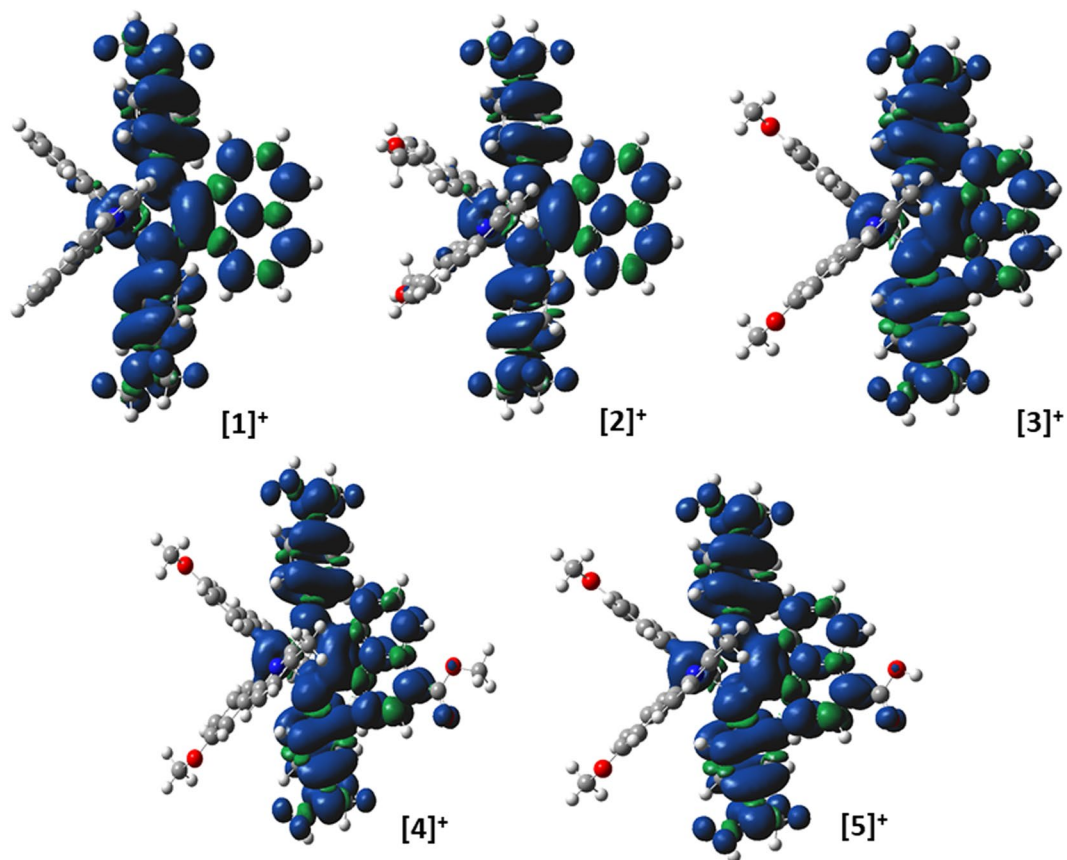
**Figure 7.** Transient (a) absorption and (b) emission spectra of 0.050 mM solutions of **4** collected in DCM at 298 K. (c) Steady-state photoluminescence spectra of a 0.050 mM solution of **4** collected in DCM at 298 K.

mixed MLCT/ILCT/LLCT transitions, thus leading to sufficiently long-lived, radiative singlet photoexcited states. There was little solvent dependence observed for **4** (Fig. 7 and Supplementary Fig. S30), suggesting that ligand dissociation or exciplex formation with MeCN did not occur upon photoexcitation. Gratifyingly too, these observations validate our attempts to improve the excited state photophysical properties, grafting abilities, and applicability of the Ar-BIAN Ir complexes in DSSCs and DSPECs.

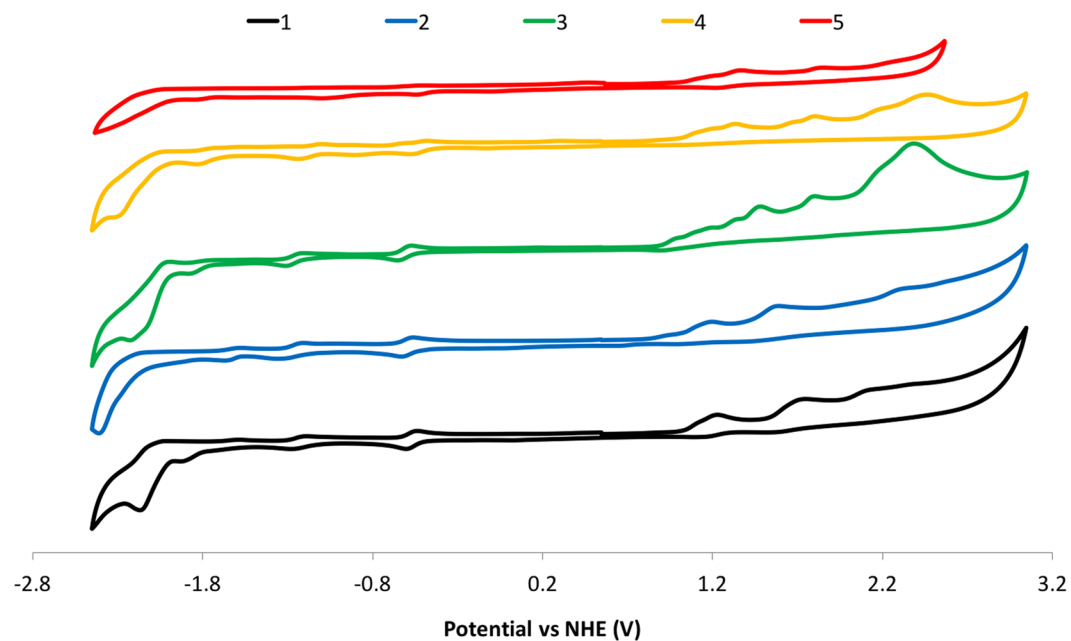
Cyclic voltammetry studies of **1–5** were conducted in order to further probe their ground state electronic behavior. The cyclic voltammograms (CVs) are shown in Fig. 9 and the observed redox couples are summarised in Table 2. The CV of **1**, previously reported by us<sup>20</sup>, exhibits a reversible first reduction wave at  $-0.57$  V versus NHE and a second quasi-reversible wave at  $-1.23$  V, both ascribed to reduction of the Ar-BIAN ligand. The series of oxidation waves in **1** are all irreversible. We had previously assigned the first oxidation wave at  $1.22$  V to be localised on the *N,N*-dimethylaniline fragment, while the second oxidation consisted of contributions from the C<sup>^</sup>N ligands and the Ir<sup>IV</sup>/Ir<sup>III</sup> redox couple. The incorporation of an electron-donating MeO group leads to a cathodic shift in both the reduction and oxidation waves<sup>20,21,24,37</sup>. The oxidation waves are more substantively affected with substitution at the 3-position resulting in a  $0.13$  V shift of  $E_{ox}^1$  to lower potential in **3** compared to a more modest  $0.03$  V shift in **2** with the 4MeO-5Meppy C<sup>^</sup>N ligand. The lower energies calculated for the HOMO of **2** ( $E_{HOMO} = -5.18$  eV) compared to that of **3** ( $E_{HOMO} = -5.15$  eV) are in good agreement with the higher anodic potentials measured for **2** compared to that of **3** (Table 2). Addition of the electron-withdrawing ester functionality in **4** results in an anodic shift of both the oxidation and the reduction waves. Hydrolysis of the ester to a carboxylic acid as in **5** anodically shifts  $E_{ox}^1$  further to  $1.33$  V, but does not dramatically affect  $E_{red}^1$ . Thus, peripheral substitution of the iridium complexes in **2–5** does not appear to alter the nature of the first oxidation and reduction processes. In comparison, the important redox processes in the N3 dye in methanol are found at  $1.13$  and  $-0.89$  V, resulting in an electrochemical gap of  $2.02$  V, which is significantly larger than that found experimentally for **5**<sup>7</sup>.

## Conclusions

Overall, we have presented a series of five panchromatic iridium complexes (four of which are new) coordinated by Ar-BIAN ligands. The Ir complexes have absorption profiles that surpass the renowned N3 dye, and both the electrochemical measurements and DFT calculations support the existence of MLCT, LLCT, and ILCT mixed



**Figure 8.** Triplet spin density distributions of complexes 1–5, obtained from DFT calculations with the UB3LYP/SBKJC-VDZ basis set for Ir(III) and 6–31 G\*\* for C, H, N, and O, using a CPCM (MeCN) solvent model. The contours are isovalued at 0.004.



**Figure 9.** CV traces for 1–5 recorded at 298 K at 50 mV/s in MeCN solution with 0.10 M (n-Bu<sub>4</sub>N)PF<sub>6</sub> as the supporting electrolyte.

Compound	$E_{1/2}/V$ vs NHE ( $\Delta E_p/mV$ ) <sup>a</sup>				$\Delta E^d/V$	$E_{HOMO}^e/eV$	$E_{LUMO}^e/eV$	$ \Delta E_{H-L} ^f/eV$	$E_{0,0}^g/eV$	$E(S^+/S^*)^h/V$
	$E_{ox}^1$	$E_{ox}^2$	$E_{red}^1$	$E_{red}^2$						
1	1.22 <sup>b</sup>	1.73 <sup>b</sup>	-0.57 (70) <sup>c</sup>	-1.23 (60) <sup>b</sup>	1.82	-5.19	-2.91	2.28	1.66	-0.44
2	1.19 <sup>b</sup>	1.57 <sup>b</sup>	-0.60 (65) <sup>c</sup>	-1.28 (131) <sup>b</sup>	1.82	-5.18	-2.89	2.29	1.60	-0.41
3	1.09 <sup>b</sup>	1.51 <sup>b</sup>	-0.61 (75) <sup>c</sup>	-1.28 (65) <sup>b</sup>	1.74	-5.15	-2.89	2.26	1.66	-0.57
4	1.21 <sup>b</sup>	1.38 <sup>b</sup>	-0.53 (81) <sup>c</sup>	-1.17 (127) <sup>b</sup>	1.77	-5.18	-3.04	2.14	1.55	-0.34
5	1.33 <sup>b</sup>	1.83 <sup>b</sup>	-0.52 (78) <sup>b</sup>	-1.05 <sup>h</sup>	1.89	-5.18	-3.06	2.12	1.55	-0.27

**Table 2.** Summary of electrochemical data for 1–5. <sup>a</sup>CV traces recorded at 298 K at 50 mV/s in MeCN solution with 0.1 M (n-Bu<sub>4</sub>N)PF<sub>6</sub>. Values are in V vs. NHE (Fc<sup>+</sup>/Fc vs. NHE = 0.63 V). The numbers in parentheses refer to  $\Delta E_p$ , which is the difference between the anodic and cathodic peak potentials<sup>38</sup>. A non-aqueous Ag<sup>+</sup>/Ag electrode (silver wire in a solution of 0.1 M AgNO<sub>3</sub> in MeCN) was used as the pseudo reference electrode; a glassy-carbon electrode was used for the working electrode, and a Pt electrode was used as the counter electrode. <sup>b</sup>Irreversible.  $E_{pa}$  reported for oxidation peak potentials and  $E_{pc}$  for reduction peak potentials. <sup>c</sup>Quasireversible.  $\Delta E = \Delta E_{redox} = E_{ox}^1(pa) - E_{red}^1(pc)$ . Note that the  $E_{ox}^1(pa)$  and  $E_{red}^1(pc)$  are distinct from  $E_{1ox}$  and  $E_{1red}$ , respectively, in the table since the latter are averaged values for the quasi-reversible redox waves. <sup>d</sup>DFT calculations were performed with the B3LYP/SBKJC-VDZ basis set for Ir(III) and 6–31 G\*\* for C, H, N, and O, using a CPCM (MeCN) solvent model. <sup>e</sup> $E_{0,0}$  is estimated from the onset of the absorption spectrum at ca. 10% intensity. <sup>g</sup>Calculated from  $E(S^+/S^*) = E(S^+/S) - E_{0,0}$ . <sup>h</sup> $E_{red}^2$  (pc).

states that account for the low energy optical absorption bands. Most significantly, in contrast to traditional solution methods, mechanochemical ball milling enabled the synthesis of new Ar-BIAN ligands in which ester and carboxylate functionalities are present at the bay region of the acenaphthene motif. This increases the ligands'  $\pi$ -accepting capacities and imparts grafting capabilities to our iridium complexes. Our ongoing efforts include the introduction of these iridium Ar-BIAN compounds into DSSCs and more generally, the creation of new Ar-BIAN copper and other metal complexes that can be incorporated into DSPECs to produce solar fuels and chemicals.

## Methods

**Compound 5-carboxy-1,2-dihydroacenaphthene, 7.** To a  $-78^\circ\text{C}$  (60 mL) solution of **6** (3.00 g, 12.8 mmol, 1.0 equiv.) in diethyl ether, 1.6 M *n*-BuLi (12 mL, 19 mmol, 1.5 equiv.) was added dropwise over 30 min. The reaction mixture was stirred an additional 30 min at  $-78^\circ\text{C}$ . The solution was then allowed to warm to RT and stirred for an additional 1 h. The reaction was quenched with dry ice and a white precipitate formed, which was separated by vacuum filtration to obtain the desired product. The crude product was purified by recrystallisation using aqueous ethanol, and collected as an off-white solid (2.51 g). **Yield:** 99%. **Mp:** 217 °C. **<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  (ppm):** 7.91 (d,  $J = 8.37$  Hz, 1H), 7.57 (d,  $J = 7.05$  Hz, 1H), 7.30 (t,  $J = 7.58$  Hz, 1H), 7.06 (t,  $J = 6.85$  Hz, 2H), 3.04 (s, 4H). **<sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  (ppm):** 171.4, 149.4, 146.7, 138.9, 130.9, 129.0, 128.8, 128.4, 121.2, 119.5, 118.6, 29.9, 29.7. **HRMS (EI, 70 eV):** [M-H]<sup>-</sup> **Calculated:** (C<sub>13</sub>H<sub>9</sub>O<sub>2</sub>) 197.0597; **Found:** 197.0603. This compound has been twice previously reported where characterisation was limited to a melting point (Mp<sup>44</sup>: 207–211 °C and Mp<sup>45</sup>: 214–218 °C).

**Compound 5-carboxymethyl-1,2-dihydroacenaphthene, 8.** To a stirred solution of **7** (3.00 g, 15.1 mmol, 1.0 equiv.) in 50 mL of MeOH cooled in an ice bath was added dropwise, SOCl<sub>2</sub> (1.8 mL, 38 mmol, 2.5 equiv.) over 30 min. The reaction mixture was then allowed to warm to RT, before it was heated to reflux for 19 h. The MeOH was evaporated under reduced pressure and H<sub>2</sub>O was then added (50 mL). The product was extracted with DCM (50 mL), and the organic phase was dried over MgSO<sub>4</sub>, filtered under vacuum, and concentrated under reduced pressure to obtain the desired product as a brownish solid (2.45 g). **Yield:** 96%. **Mp:** 74 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 8.63 (d,  $J = 8.37$  Hz, 1H), 8.29 (d,  $J = 7.35$  Hz, 1H), 7.59 (dd,  $J = 6.91, 8.56$  Hz, 1H), 7.35 (d,  $J = 6.87$  Hz, 1H), 7.30 (dd,  $J = 1.25, 7.37$  Hz, 1H) 3.99 (s, 3H), 3.42 (s, 4H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 168.1, 153.2, 146.5, 139.8, 133.3, 130.4, 130.0, 122.2, 122.1, 120.2, 118.6, 52.03, 30.7, 30.6. The characterisation matches that previously reported<sup>46,47</sup>.

**Compound 5-methylcarboxylate-1,2-dioxo-1,2-dihydroace-naphthylene, 9.** Compound **8** (1.63 g, 7.67 mmol, 1.0 equiv.) was dissolved in 50 mL of acetic anhydride at 110 °C. CrO<sub>3</sub> (6.0 g, 60 mmol, 7.8 equiv.) was added carefully to the stirred solution over a period of 1 h. The resulting green suspension was stirred at 110 °C for a further 1 h and poured onto crushed ice. Concentrated HCl (10 mL) was added and the mixture was filtered. The yellow precipitate was washed with water and dried in vacuum. The crude product ( $R_f$  of 0.15, DCM on silica) was purified by column chromatography with silica gel using MeOH/DCM (2.5:97.5%). A yellow flaky solid (1.31 g) was collected. **Yield:** 72%. **Mp:** 189 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 9.32 (dd,  $J = 8.68, 19.9$  Hz, 1H), 8.58 (m, 2H), 8.16 (dd,  $J = 7.16, 29.0$  Hz, 1H), 7.95 (m, 1H), 4.08 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 188.2, 187.4, 166.2, 145.9, 132.9, 132.5, 132.0, 131.2, 130.3, 129.7, 129.3, 122.8, 121.0, 53.0. **HR-MS (EI, 70 eV):** [M + Na]<sup>+</sup> **Calculated:** (C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>Na) 263.0315; **Found:** 263.0324.

**Compound (1E,2E)-methyl-1,2-bis((4-(dimethylamino)phen-yl)imino)-1,2-dihydroacenaph-thylene-5-carboxylate, 4-Me<sub>2</sub>N Ph-CO<sub>2</sub>MeBIAN, 12.** A stainless steel grinder jar was dried in an oven at 120 °C overnight prior to use. The grinder jar was charged with **9** (0.072 g, 0.30 mmol), *N,N*-dimethyl-4-phenylenediamine (0.094 g, 0.67 mmol), acetic acid (4.3  $\mu$ L, 0.075 mmol, 25 mol%), and Na<sub>2</sub>SO<sub>4</sub> (0.043 g, 0.30 mmol), and equipped with a 10 mm stainless steel ball. The contents in the jar were then ground



for 4 h at 30 Hz. The resultant purple gel was suspended in dichloromethane (DCM), filtered, and the filtrate was concentrated to dryness and rinsed with cyclohexane. The purple residue was recrystallised from diethyl ether (Et<sub>2</sub>O) and the isolated yield was 0.054 g (41%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.90 (d, *J* = 8.4 Hz, 1 H), 8.16 (d, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 8.0 Hz, 1 H), 7.32–7.35 (m, 2 H), 7.10–7.14 (m, 4 H), 6.82–6.86 (m, 4 H), 3.99 (s, 3 H), 3.04 (s, 6 H), 3.03 (s, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 166.9, 160.3, 159.7, 148.8, 148.5, 141.6, 141.5, 141.2, 133.3, 132.0, 130.0, 129.7, 129.3, 128.2, 127.2, 123.7, 121.9, 120.8, 120.5, 113.4, 113.1, 52.4, 41.1, 41.0. HRMS (ESI +, *m/z*): [M + H]<sup>+</sup> Calculated: (C<sub>30</sub>H<sub>29</sub>N<sub>4</sub>O<sub>2</sub>) 477.2291; Found 477.2268. Anal. Calcd. for C<sub>30</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>: C, 75.61; H, 5.92; N, 11.76; Found: C, 75.89; H, 5.57; N, 11.29.

**General procedure for the synthesis of Ir(III) bis[(C<sup>^</sup>N)-N, C<sup>2</sup>]-N, N'-bis(phenylimino)acenaphthene (Ar-BIAN) hexafluoro-phosphate complexes 1–4.** The iridium(III) dimer [(C<sup>^</sup>N)<sub>2</sub>Ir(μ-Cl)]<sub>2</sub> (0.080 mmol, 1.0 equiv.) and bis(arylimino)acenaphthene (Ar-BIAN) ligand (0.16 mmol, 2.0 equiv.) were solubilised in 12 mL of dry DCM. The mixture was degassed repeatedly, placed under N<sub>2</sub>, and heated to 50 °C for 19 h. Over the course of the reaction, the mixture darkened in color from the initial yellow. The solution was cooled to RT and the solvent was removed under reduced pressure. The crude solid was re-dissolved in a minimum amount of MeOH and added slowly to an aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (10 mL, 6.13 mmol, 1 g/10 mL) under gentle stirring. The first drop caused the precipitation of a dark-colored solid. The solid suspension was conserved at 0 °C for 2 h, collected on a Buchner funnel, and the resulting solid was washed with water and Et<sub>2</sub>O. The residue was dried *in vacuo* to obtain a dark brown/green solid. The complexes were then crystallised in dichloromethane/diisopropylether (50:50) by slow evaporation. Complexes 1–4 were obtained using this protocol.

**Iridium(III) bis[2-phenyl-pyridinato-N, C<sup>2</sup>]-N, N'-bis(4-N, N-di-methylphenylimino)acenaphthenehexafluorophosphate: [Ir(ppy)<sub>2</sub>(4-NMe<sub>2</sub>PhBIAN)]<sup>+</sup>(PF<sub>6</sub>)<sup>-</sup>, 1.** Black crystals (0.146 g). Yield: 86%. The characterization matches that previously reported<sup>21</sup>.

Iridium(III) bis[4-methoxy-2-phenyl-5-methylpyridinato-N, C<sup>2</sup>]-N, N'-bis(4-N, N-dimethyl-phenylimino)acenaphthene hexafluorophosphate: [Ir(4-MeO-5-Me-ppy)<sub>2</sub>(4-NMe<sub>2</sub>Ph-BI-AN)]<sup>+</sup>(PF<sub>6</sub>)<sup>-</sup>, 2: Black crystals (0.073 g). Yield: 80%. Mp: 337–339 °C (turned into dark liquid). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ (ppm): 8.39–8.34 (m, 2 H), 8.21 (d, *J* = 8.2 Hz, 2 H), 7.68 (d, *J* = 1.5 Hz, 2 H), 7.65 (s, 2 H), 7.57–7.53 (m, 2 H), 7.44 (d, *J* = 7.3 Hz, 2 H), 7.32 (d, *J* = 8.6 Hz, 2 H), 6.36 (dd, *J* = 8.6, 2.6 Hz, 10 H), 5.45 (s, 2 H), 3.50 (s, 6 H), 2.89 (s, 12 H), 2.28 (s, 6 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm): 169.74, 165.16, 160.15, 150.75, 150.45, 148.60, 144.51, 143.45, 139.26, 136.83, 134.17, 132.07, 131.81, 130.68, 128.89, 127.70, 125.37, 123.54, 118.36, 117.32, 111.34, 107.02, 54.96, 40.51, 18.62. HRMS (EI, 70 eV): [M-PF<sub>6</sub>]<sup>+</sup> Calculated: (C<sub>54</sub>H<sub>50</sub>IrN<sub>6</sub>O<sub>2</sub>) 1007.3623; Found: 1007.3646.

**Iridium(III) bis[3-methoxy-2-phenyl-5-methylpyridinato-N, C<sup>2</sup>]-N, N'-bis(4-N, N-dimethyl-phenylimino)acenaphthene hexafluorophosphate: [Ir(3-MeO-5-Me-ppy)<sub>2</sub>(4-NMe<sub>2</sub>Ph-BIAN)]<sup>+</sup>(PF<sub>6</sub>)<sup>-</sup>, 3.** Black crystals (0.116 g). Yield: 80%. Mp: 354 °C (turned into dark liquid). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ (ppm): 8.41 (d, *J* = 1.7 Hz, 2 H), 8.21 (d, *J* = 8.2 Hz, 2 H), 7.78–7.67 (m, 5 H), 7.55 (t, *J* = 7.8 Hz, 2 H), 7.47 (d, *J* = 7.3 Hz, 2 H), 6.95 (d, *J* = 2.7 Hz, 2 H), 6.43–6.27 (m, 8 H), 5.90 (d, *J* = 8.3 Hz, 2 H), 5.45 (s, 1 H), 3.66 (s, 6 H), 2.89 (s, 12 H), 2.30 (s, 6 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm): 169.79, 165.25, 156.29, 150.33, 149.15, 144.46, 143.53, 139.30, 138.46, 134.04, 133.52, 131.82, 131.73, 130.58, 128.87, 127.81, 123.46, 119.11, 116.78, 111.33, 109.21, 55.63, 40.47, 18.67. HRMS (EI, 70 eV): [M-PF<sub>6</sub>]<sup>+</sup> Calculated: (C<sub>54</sub>H<sub>50</sub>IrN<sub>6</sub>O<sub>2</sub>) 1007.3623; Found: 1007.3625.

**Iridium(III) methyl-bis[3-methoxy-2-phenyl-5-methyl-pyridinato-N, C<sup>2</sup>]-N, N'-bis(4-N, N-di-methylphenyl-imino)acenaphthene-5-carboxylate hexafluorophosphate: [Ir(3-MeO-5-Me-ppy)<sub>2</sub>(4-NMe<sub>2</sub>Ph-BIAN-CO<sub>2</sub>Me)]<sup>+</sup>(PF<sub>6</sub>)<sup>-</sup>, 4.** Black crystals (0.095 g). Yield: 73%. Mp: 353–355 °C (turned into dark liquid). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ (ppm): 9.07 (dd, *J* = 8.7, 0.7 Hz, 1 H), 8.41 (dd, *J* = 1.9, 1.0 Hz, 2 H), 8.22 (d, *J* = 7.7 Hz, 1 H), 7.78–7.72 (m, 4 H), 7.67 (dd, *J* = 8.7, 7.4 Hz, 2 H), 7.63–7.57 (m, 2 H), 7.57–7.52 (m, 1 H), 6.98 (d, *J* = 2.6 Hz, 2 H), 6.52–6.05 (m, 8 H), 5.92 (dd, *J* = 9.8, 8.3 Hz, 2 H), 3.99 (s, 3 H), 3.69 (d, *J* = 2.4 Hz, 6 H), 2.93 (d, *J* = 5.7 Hz, 12 H), 2.33 (s, 6 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm): 169.25, 168.03, 166.52, 165.14, 156.40, 150.70, 150.40, 149.10, 149.03, 144.37, 143.58, 143.51, 139.46, 139.40, 138.09, 133.94, 133.64, 132.93, 131.93, 131.75, 131.73, 130.43, 130.35, 130.11, 128.50, 128.35, 123.58, 121.78, 119.17, 116.85, 116.79, 111.28, 111.20, 109.19, 55.63, 52.84, 40.45, 40.42, 18.65. HRMS (EI, 70 eV): [M-PF<sub>6</sub>]<sup>+</sup> Calculated: (C<sub>56</sub>H<sub>52</sub>IrN<sub>6</sub>O<sub>4</sub>) 1065.3678; Found: 1065.3668.

Synthesis of Ir(III) bis[3-methoxy-2-phenyl-5-methylpyridinato-N, C<sup>2</sup>]-N, N'-bis(4-N, N-dimethylphenyl-imino)acenaphthene-5-carboxylate hexafluorophosphate, 5: Complex [Ir(3-MeO-5-Me-ppy)<sub>2</sub>(4-NMe<sub>2</sub>Ph-BIAN-CO<sub>2</sub>Me)]<sup>+</sup>(PF<sub>6</sub>)<sup>-</sup> (4) (0.050 g, 0.040 mmol, 1.0 equiv.) and NaOH (0.0050 g, 0.12 mmol, 2.7 equiv.) were dissolved with 6 mL H<sub>2</sub>O and 6 mL MeCN. The mixture was degassed three times, placed under N<sub>2</sub>, and heated to 85 °C for 22 h. The solution was cooled to RT and quenched with 1.2 mL of 0.10 N aqueous HCl. After careful removal of the solvent, the product was extracted with DCM (3 × 15 mL), evaporated to dryness, and the crude solid was re-dissolved in a minimum amount of MeOH. To this solution was slowly added a solution of NH<sub>4</sub>PF<sub>6</sub> (10 mL, 6.13 mmol, 1 g/10 mL) under gentle stirring. Upon the first drop addition of aqueous NH<sub>4</sub>PF<sub>6</sub> solution, the appearance of a greenish black precipitate was observed and continued until the addition was complete. Then, the greenish black solid suspension was conserved for 3 h at 0 °C and collected by a Buchner funnel filtration following washing with water and Et<sub>2</sub>O. The resulting residue was dried *in vacuo* to obtain a greenish dark solid powder. The crude product was recrystallised in dichloromethane/diisopropylether (50:50) by slow evaporation to obtain greenish black crystals. Greenish black crystals (0.047 g). Yield: 96%. Mp: 359–360 °C (turned into dark liquid). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ (ppm): 9.12 (d, *J* = 8.6 Hz, 1 H), 8.42 (bs, 2 H), 8.25 (d, *J* = 7.7 Hz, 1 H), 7.76 (d, *J* = 2.1 Hz, 5 H), 7.65 (m, 2 H), 7.60–7.52 (m, 2 H), 6.98 (d, *J* = 2.6 Hz, 2 H),

6.47–6.24 (m, 8H), 5.97–5.88 (m, 2H), 3.69 (d,  $J = 1.7$  Hz, 6H), 2.94 (s, 12H), 2.33 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  (ppm): 170.44, 169.38, 166.52, 164.41, 156.27, 150.49, 150.29, 144.72, 144.10, 144.06, 139.16, 137.92, 137.88, 134.23, 134.19, 132.74, 132.58, 130.10, 130.02, 129.41, 128.99, 128.09, 127.04, 123.21, 121.59, 118.90, 118.89, 115.86, 115.83, 111.13, 111.11, 109.99, 108.97, 54.99, 39.61, 39.58, 17.33, 17.31. HR-MS (EI, 70 eV):  $[\text{M-PF}_6]^+$  Calculated:  $(\text{C}_{55}\text{H}_{50}\text{IrN}_6\text{O}_4)$  1051.3521; Found: 1051.3519.

**Data availability.** Supplementary Information available: General procedures, experimental details, photo-physical and electrochemical characterisation protocols,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and computational details. The data supporting this study are available at: <http://dx.doi.org/10.17630/c28fddad-6877-4c31-80fa-f88600b735ae>.

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## Author Contributions

K. Hasan contributed to the synthesis of all the iridium complexes, UV-vis measurements, and cyclic voltammetry studies. J. Wang contributed to the synthesis of ester functionalised Ar-BIAN ligand, steady-state photoluminescence measurements, and time-resolved transient spectroscopic studies. A.K. Pal contributed to the synthesis of the complexes and DFT calculations for all the compounds. C. Hierlinger contributed to the synthesis of complexes. E. Zysman-Colman, F. Garcia, and H.S. Soo planned and designed the experiments. All authors contributed to writing and editing the manuscript.

## Additional Information

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