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Panchromic Cationic Iridium(III) Complexes

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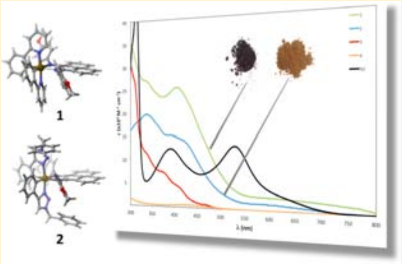
Supporting Information

ABSTRACT: We report the synthesis, X-ray structures, and optoelectronic characterization of two cationic iridium complexes bearing bis[(4-methoxyphenyl)-imino]acenaphthene ligands. These complexes exhibited panchromic absorption extending as far as 800 nm, making them of interest for solar-energy-harvesting applications.



INTRODUCTION

Two main strategic efforts are underway in the quest to efficiently harness solar energy: photovoltaic devices (PVDs), which create current directly from sunlight,[1] and water-splitting (WS) systems, which incorporate one or more photosensitizers to catalyze the production of H_2 and O_2 from water.[2] One of the most promising strategies for PVDs is the incorporation of benign photosensitizer molecules that act to efficiently harvest solar energy. The two most promising technologies for commercialization and large-scale use in this respect are organic solar cells and dye-sensitized solar cells (DSSCs);[3] however, both of these technologies have only advanced slowly over the past decade in spite of enormous resources being allocated to photovoltaic energy research. Many of the most efficient DSSCs to date are based on a heteroleptic ruthenium dye $[Ru(dcbpy)_2(NCS)_2]$ [known as **N3**, where dcbpy = bis(4,4′-dicarboxy-2,2′-bipyridine)],[4] the best of which, developed by Sharp Corp., has a power conversion efficiency (η) of 11.2%, only around 3% higher than that reported for **N3** nearly 20 years earlier;[5] the highest performing DSSC in the laboratory with 12.3% at 1 Sun contains both a porphyrinic and an organic dye.[6]

The incorporation of iridium(III) photosensitizers (dyes) onto semiconductor surfaces in the context of a DSSC is of particular interest because of their higher thermal and chemical stability compared to ruthenium, longer excited-state lifetimes, and comparable quantum yields for conversion of absorbed photons to current.[7] Despite the potential benefits, we know of *only six* reports in the literature for iridium-based DSSCs. Gray and co-workers first demonstrated their viability using dcbpy and dcbq (dcbq = 4,4-dicarboxy-2,2-biquinoline) ancillary ligands to red-shift the absorption spectrum.[7] Low-energy absorption features at ca. 500 nm result from ligand-to-ligand charge-transfer (^{1}LLCT) transitions, which contrasts them with ruthenium complexes that absorb primarily from a metal-to-ligand charge-transfer (^{1}MLCT) state. Reported DSSC efficiencies (η) were less than 1%. Tridentate iridium complexes of the form $[Ir(C\text{^}N\text{^}C)(tpy\text{-}CO_2H)]$, recently proposed by Nakabayashi and co-workers,[8] show low-energy absorption bands centered at around 512 nm that are mixed ^{1}LLCT/^{1}MLCT transitions. Using an architecture similar to that of Gray and co-workers, Dragonetti and co-workers and Tian and co-workers have each recently obtained photosensitizers absorbing only out to 550 nm from the same type of mixed ^{1}MLCT/^{1}LLCT transitions.[9] The DSSC performance was thus poor ($\eta \leq 2.86\%$). Finally, Nazeeruddin and co-workers[10] reported six iridium dyes with a maximum η among them of 2.51%. In each of these cases, the absorption profile was not sufficiently red-shifted in order for the dye to act as an efficient harvester of sunlight (i.e., J_{sc} is low), an issue echoed with the iridium photosensitizers used for WS.[9a,11] A survey of red-emitting cationic iridium complexes, all of which incorporate highly conjugative bidentate cyclometallating (C^N) and/or ancillary (N^N) ligands, reveals that very few absorb light past 550 nm.[12]

The use of bis(arylimino)acenaphthene (Ar-BIAN) ligands for catalysis[13] and metal-mediated olefin polymerization[14] has been quite extensively investigated along with their coordination chemistry to main-group atoms,[15] d-block metals, and lanthanides.[16] Despite the facility to modulate the electronics of the ligand, ease of synthesis, and low cost, the optoelectronic properties of complexes bearing BIAN ligands have been only modestly studied.[17] Indeed, Adams, Weinstein, and Castellano have all shown that the charge-transfer (CT) absorption and emission bands in platinum acetylide complexes can be significantly bathochromically shifted into the red and near-IR with incorporation of an Ar-BIAN unit.[18a−c] The observed red shift is due to the greatly stabilized π^* LUMO localized on the conjugated Ar-BIAN. Apart from the rigidity of the acenaphthene unit and the steric protection of the metal conferred by the pendant aryl groups, which mitigate nonradiative decay pathways, Ar-BIAN ligands are redox-active bidentate chelates capable of storing up to four electrons over

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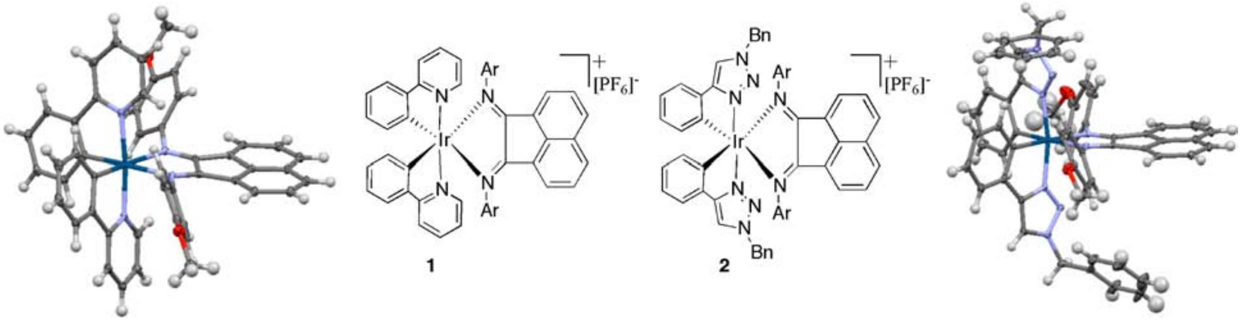

Figure 1. Complexes in the study, [(ppy)$_2$Ir(4-MeOPh-BIAN)]PF$_6$ (**1**) and [(phtl)$_2$Ir(4-MeOPh-BIAN)]PF$_6$ (**2**), along with ORTEP perspective representations (ellipsoids at 30% probability). The counterion has been removed for clarity. Ar = 4-MeOPh.

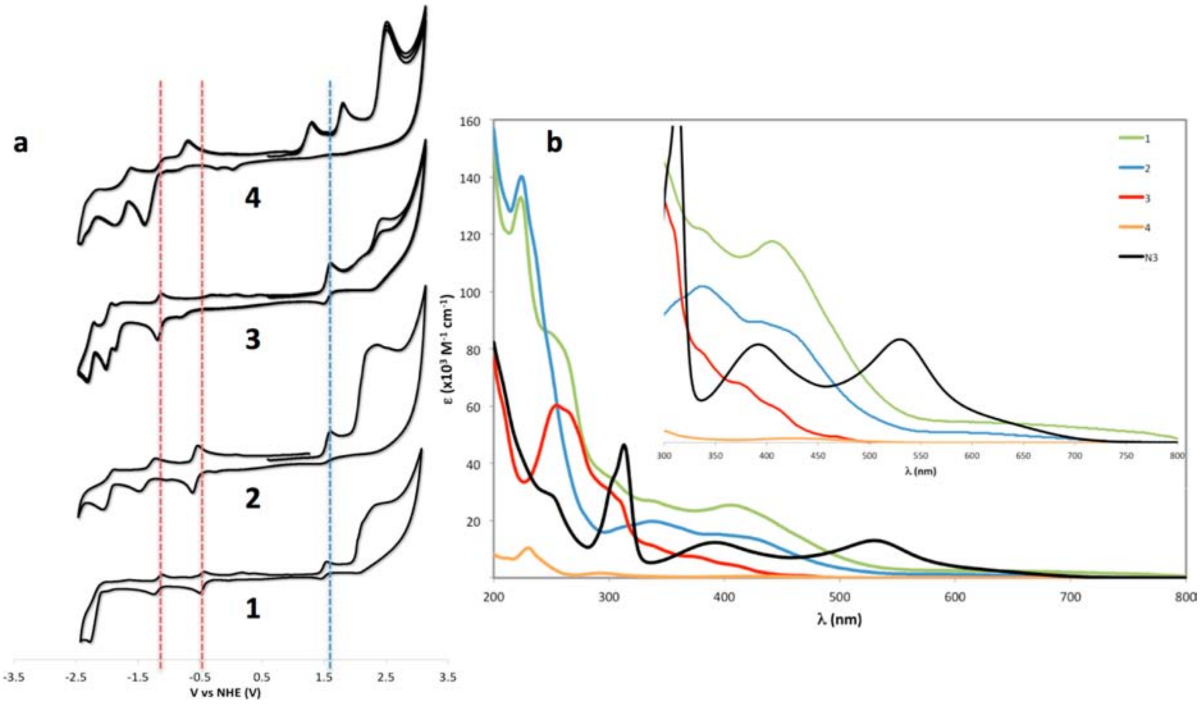

Figure 2. (a) Cyclic voltammograms for **1**−**4** (V vs NHE) recorded at room temperature at 50 mV/s in ACN with 0.1 M (^{n}Bu$_4$N)PF$_6$. Vertical dotted lines highlight the relative positions of first oxidation and first and second reduction waves with respect to **1**. (b) UV−vis spectra for **1**−**4** in ACN at 298 K. UV−vis spectrum for **N3** in MeOH at 298 K. Inset: Zoomed UV−vis spectra for the low-energy region.

consecutive reductions.[19] Thus, with the aim of developing panchromic iridium complexes more capable of harnessing sunlight, we report the synthesis and physical and optoelectronic studies of the first two examples of iridium(III) complexes bearing Ar-BIAN ligands (Ar = 4-MeOPh).[20]

■ RESULTS AND DISCUSSION

The properties of these two complexes, with either ppy (ppyH = 2-phenylpyridine, **1**) or phtl (phtl = 1-benzyl-4-phenyl-1*H*-1,2,3-triazole, **2**) C^N ligands, are contrasted with those of archetypal [(ppy)$_2$Ir(bpy)]PF$_6$ (**3**), where bpy = 2,2′-bipyridine (Figure 1).

Red-colored 4-MeOPh-BIAN (**4**) was obtained in 41% yield through ZnCl$_2$-catalyzed condensation of *p*-anisidine with acenaphthenequinone, followed by demetalation with sodium oxalate.[13b,21] Owing to the hydrophobicity of **4**, cleavage of [Ir(ppy)$_2$Cl]$_2$ was accomplished in refluxing dichloromethane (DCM) to afford **1** in excellent yield (96%), as opposed to the more commonly employed alcoholic solvents. Complex **2** was obtained in 48% yield from phtl and IrCl$_3$, following our one-pot two-step protocol.[22] Both complexes are air-stable and were isolated as their PF$_6$$^-$ salts, following an anion metathesis of the Cl$^-$ complexes with aqueous NH$_4$PF$_6$. The structural identity and purity for **1**, **2**, and **4** were ascertained through ^{1}H and ^{13}C NMR, electrospray ionization high-reslution mass spectrometry, and melting point analyses (see the Supporting Information). Additionally, dark-brown-to-black-colored prism-like X-ray-quality crystals for both **1** and **2** were grown through the slow evaporation of a 1:1 mixed (^{i}Pr)$_2$O and DCM solution. The complexes each possess a pseudooctahedral geometry with the nitrogen atoms of the C^N ligand in a trans disposition with average (N−Ir−N)$_{\mathrm{BIAN}}$ and (C−Ir−N)$_{\hat{\mathrm{C}}\mathrm{N}}$ bond angles of 76° and 80°, respectively. The Ir−N$_{\hat{\mathrm{C}}\mathrm{N}}$, Ir−C$_{\hat{\mathrm{C}}\mathrm{N}}$, and Ir−N$_{\mathrm{BIAN}}$ bond lengths are unremarkable compared to those of **3**,[23] although there is a slight elongation in the latter bond in **1** (2.171 Å) compared to **2** (2.146 Å). The 4-anisyl groups of the BIAN ligand are twisted by 63° and 67° respectively for **1** and **2** with respect to the least-squares plane described by the rings of the acenaphthene moiety. The torsion of these rings promotes an intramolecular π-stacking interaction

Table 1. Relevant Spectroscopic and Electrochemical Data for 1−4

		$E_{1/2}$/V[a] vs NHE (ΔE_p/mV)				
	λ_{abs}/nm[b] (ε/10^4 M^{-1} cm^{-1})	E_{ox}	E_{red}	ΔE/V	$E_{0,0}$/eV	$E(S^+/S^*)$/V[c]
1	224 (13.25), 255 (8.32), 306 (3.35), 336 (2.70), 406 (2.54), 630 (0.25)	1.50 (76)	−0.47 (62)	1.97	1.55	−0.05
2	224 (14.01), 336 (1.97), 390 (1.53), 570 (0.13)	1.56[d]	−0.57 (75)	2.07	1.70	−0.20
3	253 (6.0), 310 (2.66), 341 (1.08), 375 (0.74), 410 (0.43), 465 (0.08)	1.52 (88)	−1.14 (55)	2.66	2.49	−0.97
4	230 (10.46), 292 (1.61), 425 (0.53)	1.26[d]	−0.69[d]	1.95	2.40	−1.14

[a] Recorded in N_2-saturated ACN with 0.1 M (^{n}Bu$_4$N)PF$_6$ and referenced internally to Fc/Fc$^+$ at a scan rate of 50 mV/s. Values are versus NHE (Fc/Fc$^+$ vs NHE = 0.63 V).[24] Only first oxidation and reduction peaks are shown. $\Delta E = \Delta E_{redox}$. [b] Recorded in air-equilibrated ACN at 298 K. [c] Calculated from $E(S^+/S^*) = E(S^+/S) - E_{0,0}$, where $E_{0,0}$ is estimated from the onset of the absorption spectrum at ca. 10% intensity. [d] Irreversible. $E_{p,a}$ reported.

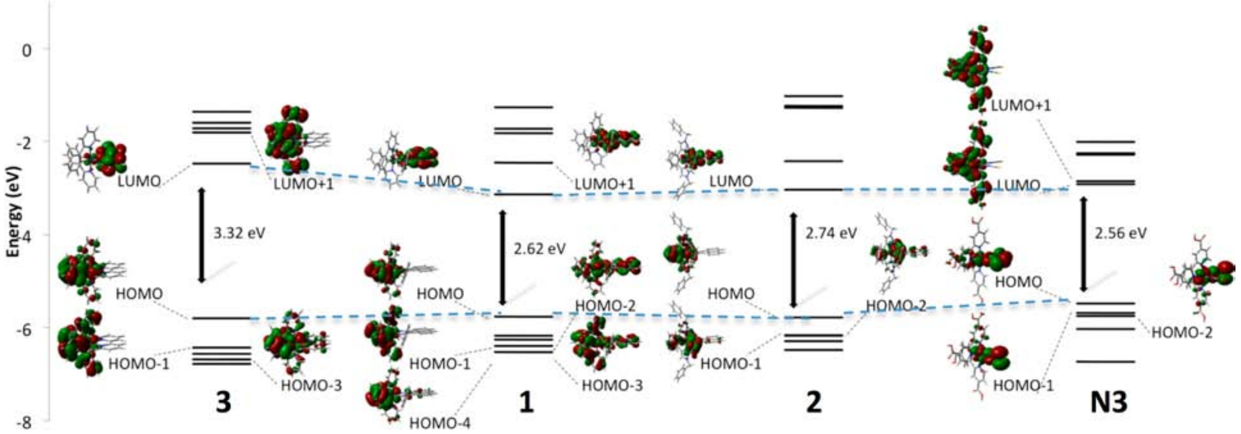

Figure 3. Energy diagram and isodensity surface plots of the relevant frontier MOs (HOMO−4 to LUMO+4) for **1**−**3** and **N3** (0.02 isovalue).

with the phenyl ring of the C^N ligand. Indeed, the average distances between the centroid of the phenyl ring of the C^N ligand and the least-squares plane of the anisyl rings are 3.525 and 3.701 Å respectively for **1** and **2**.

The electrochemical behavior for **1** and **2** was evaluated by cyclic voltammetry (CV) using Fc/Fc$^+$ as an internal standard and referenced to NHE [Fc/Fc$^+$ = 0.63 V in acetonitrile (ACN)].[24] CV scans were found to be reproducible irrespective of the scan rate (50−200 mV/s). Their CV properties were compared to reference compounds **3** and **4** (Figure 2a), with data listed in Table 1. The CV for **4** is a complex series of irreversible oxidation and reduction waves. In contrast and similar to **3** ($E_{1/2,ox}$ = 1.52 V), the first oxidation waves, corresponding to the one-electron Ir^{III}/Ir^{IV} couple, for **1** and **2** were at 1.50 and 1.56 V, respectively.[25] The marked decreased reversibility of this wave in **2** points to the increased ligand contribution from the phtl ligand compared to that for ppy. The first reduction waves for each of **1** and **2** are centered on BIAN, are quasi-reversible, and are found at −0.47 and −0.57 V, respectively, significantly anodically shifted compared to that of **3** ($E_{1/2,red}$ = −1.14 V), attributed to the increased conjugation imparted by BIAN. The expected 100 mV destabilization of the LUMO for **2** compared to **1** is due to the electronic influence of phtl.[22] Additionally, there are second quasi-reversible reduction waves at −1.18 and −1.32 V, respectively, for **1** and **2**, attributed by density functional theory (DFT) calculations to a further reduction of BIAN. Reduction of the ppy ligand, as demonstrated clearly in **3**, occurs only at −2.20 V (in **1** $E_{1/2,red}$ = −2.16 V). The resulting ΔE_{redox} values for **1** and **2** are thus 1.97 and 2.07 V, respectively, significantly smaller than that for **3** at 2.66 V. The first oxidation and reduction processes for reference dye **N3** in methanol (MeOH) were estimated to be at 1.13 and −0.89 V, respectively, for an electrochemical gap of 2.02 V.[26] Thus, while the redox gaps are similar for the three complexes, the first oxidation and reduction potentials for **1** and **2** are stabilized by around 370 mV. The E_{ox} values are compatible with the energy requirements for operation of a DSSC using an I^-/I_3^- electrolyte system.[1a] Importantly, the excited-state oxidation potentials, $E(S^+/S^*)$, are not sufficiently negative (<−0.5 V) to efficiently inject into the conducting band of TiO_2 (E_{cb} ∼ −0.5 V). Thus, judicious decoration of the C^N ligands will be required to raise the energy of the HOMO and thus the excited-state oxidation potential. It is also evident that acid groups will need to be incorporated to permit adsorption onto TiO_2 for these complexes to be incorporated into a DSSC. Current efforts are underway to address these design criteria.

The absorption spectra for **1** and **2**, along with ligand **4** and two benchmark complexes, **3** and **N3**, are depicted in Figure 2b and the data collected in Table 1. Ligand **4** is a red solid owing to the $\pi-\pi^*$ transition centered at 425 nm. The molar absorptivities (ε) for **4** are significantly lower compared to the complexes. Typical of many iridium complexes, the absorption profile for **3** tails off at 450 nm. Low-energy transitions are ascribed to mixed CT processes, while higher intensity bands between 200 and 300 nm are attributed to ligand-centered (LC) transitions.[23,25b] For both **1** and **2**, the CT bands are more absorptive compared to **3** and, notably, extend to 800 and 700 nm, respectively. Not surprisingly and consistent with the CV data, the absorption for **2** is blue-shifted compared to **1** because we had previously shown that aryltriazoles destabilize both the HOMO and LUMO, the latter to a greater extent, thus increasing the HOMO−LUMO gap.[22] To put the absorbing capacity of **1** and **2** into perspective, we compared the integrated product of ε with the AM 1.5 solar irradiance spectrum over the range of 400−800 nm (thus, smaller than the band gap of 3.2 eV for TiO_2)[27] for **1**−**3** versus **N3**. As expected, **3** absorbs only 6% as much light as **N3**. Complexes **1** and **2**, respectively, absorb 104% and 50% as much light as **N3**. Thus, **1** is just as effective an absorber of light as **N3**!

A combined DFT/time-dependent DFT (TDDFT) study was undertaken in order to elucidate the nature of the electronic structures for **1** and **2** (see the Supporting Information for the computational protocol). The optimized ground-state structures for **1** and **2** are in close agreement with the geometries obtained from the crystallographic studies. As with **3**, their HOMOs are equally situated on both the iridium and the C^N ligand, while their LUMOs are localized over the entirety of the N^N ligand (Figure 3 and Tables S2 and S3 in the Supporting Information). The LUMO+1 is also BIAN-based but concentrated on the acenaphthene core. The increased conjugation present in BIAN results in a large stabilization of both the LUMO and LUMO+1 orbitals compared to **3**. Replacement of the ppy ligands for phtl ligands results in a net increase in the HOMO−LUMO gap due to greater destabilization of the LUMO than the HOMO. Compared to **N3**, the HOMO−LUMO gaps for **1** and **2** are larger by 0.06 and 0.18 eV, respectively. The DFT assignments and relative energies of the MOs are consistent with the CV data.

From TDDFT analysis (Figures S11 and S12 and Tables S4−S7 in the Supporting Information), the predicted absorption spectra correlate well with the experiment. The low-energy absorption bands ($\lambda_{abs} > 500$ nm) for both **1** and **2** are a mixture of spin-allowed and spin-forbidden mixed $Ir(d\pi) \rightarrow \pi^*_{BIAN}$ MLCT and $\pi_{\hat{C}N} \rightarrow \pi^*_{BIAN}$ LLCT transitions, reminiscent of the CT behavior of ruthenium-based dyes such as **N3**.[28] For **2**, the absorption bands in the region of 460−500 nm also contain some intraligand CT (^{1}ILCT) character from the electron-rich 4-MeOPh groups to the electron-poor acenaphthene system. High-intensity bands between 200 and 300 nm are assigned to LC transitions, as is commonly observed for cationic iridium complexes. No emission at 298 K was detected experimentally up to 800 nm. Although this could be due to low-lying dark states, as has been reported elsewhere for iridium complexes bearing highly conjugated ligands,[12b,e] the computations point to emission in the red-to-near-IR region. Current efforts are underway to detect emission past 800 nm.

In summary, two Ir-BIAN complexes have been synthesized and characterized. The electrochemical and spectroscopic studies reveal panchromic absorption of light, making these complexes distinct from other iridium complexes. However, the energy match is suboptimal for their use as dyes in DSSCs, and further electronic tuning will be required, the results of which will be reported elsewhere. Nevertheless, this study tantalizingly opens the door to the further development of iridium-based dyes for DSSCs and even WS applications.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for **1** and **2** in CIF format, experimental procedures, complete characterization including ^{1}H and ^{13}C NMR spectra for **1**, **2**, and **4**, individual absorption spectra for **1**−**4**, and selected data from TDDFT and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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