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Introduction

The 1H-1,2,3-triazole (triazole) synthon, easily obtained in high yield through a copper-catalyzed azide-alkyne cycloaddition reaction,¹ has been exploited in myriad applications, including functional materials.² Recently, we and others have investigated the optoelectronic properties of iridium(III) complexes containing the triazole unit, which acts as a coordinating ligand. Cationic heteroleptic iridium(III) complexes incorporating 1N-alkyl(aryl)-4-aryl-1,2,3-triazoles (aryltriazoles, atl) cyclometallating (C^N) ligands,³ 1N-alkyl(aryl)-4-pyridyl-1,2,3-triazoles (pyridyltriazoles, pytl) ancillary (N^N) ligands,⁴ or both^{3b,5} have exhibited improved photoluminescent quantum efficiencies (Φ_{PL}) and bluer absorption and emission compared to their pyridine-containing congeners. The blueshifting is due to a greater destabilization of the LUMO compared to the HOMO upon replacement of the pyridine ring with a triazole moiety. Still unexplored is the incorporation of a 1,1'-alkyl(aryl)-4,4'-bi-1H-1,2,3-triazolyl (bistriazole, btl) unit as an ancillary ligand. Indeed, the btl moiety has only been fleetingly explored as a bidentate ligand for Ru,⁶ Cu^{6a,7} and Re.^{6a} Our motivation for the study of iridium complexes

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Cationic iridium(III) complexes bearing a bis(triazole) ancillary ligand†

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Three new heteroleptic cationic iridium complexes of the form $[Ir(C^N)(btl)]^+$, where btl = 1,1'-benzyl-4,4'-bi-1*H*-1,2,3-triazolyl and C^N = 2-phenylpyridine (ppyH) (1), 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (phtl) (2) or 1-benzyl-4-(2,4-difluorophenyl)-1*H*-1,2,3-triazole (dFphtl) (3), were synthesized and isolated as their hexafluorophosphate (PF₆⁻) salts and fully characterized. The single crystal structure of **3** has been solved. Along the series from 1–3 the absorption spectra shift hypsochromically while the electrochemical gap increases from 3.25 to 3.54 to 3.88 V. Acetonitrile solutions of **1** and **2** are poorly luminescent, sky-blue emitters with predominant ligand-centered and charge transfer character, respectively. Theoretical calculations support these assignments. Complex **3** is not photostable and decomposes to solvento-based structures of the form $[Ir(dFphtl)_2(ACN)_n]^+$ (n = 1, 2) through a dissociation and degradation of the btl ligand.

bearing a btl N^N ligand was to (i) systematically investigate the impact of triazole incorporation upon the optoelectronic properties of the complex and (ii) promote a further blue-shift in the emission spectrum as part of our goal of developing highly luminescent and stable deep-blue emitters.

In this report, we describe the computational study, synthesis and characterization of three btl-containing cationic iridium(m) complexes 1–3. In order to best assess the effect of the btl ancillary ligand, we contrast the properties of 1–3 with $[(ppy)_2Ir(bpy)]PF_6$ (4), $[(pht)_2Ir(bpy)]PF_6$ (5) and $[(dFpht)_2Ir(bpy)]PF_6$ (6). While computations, UV-vis spectroscopy and cyclic voltammetry (CV) indicate very large HOMO–LUMO gaps, the photophysical investigation reveals that only blue-green to sky-blue emission is obtained, underscoring the difficulty in rationally designing deep-blue phosphorescent emitters (Chart 1).

Experimental section

General procedures

Commercial chemicals were used as supplied. All experiments were carried out with freshly distilled anhydrous solvents obtained from a Pure SolvTM solvent purification system from Innovative Technologies except where specifically mentioned. Triethylamine (Et_3N) and diisopropylamine (iPr_2NH) were distilled over CaH₂ under a nitrogen atmosphere. Solvents employed for the Click reaction were used without further purification: these consisted of commercial lab grade methanol and deionised water, which was accessible in house.

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[†]Electronic supplementary information (ESI) available: ¹H NMR spectra for **btl**, **1–3**. ¹³C NMR spectra for **btl**, **1–2**. ¹⁹F NMR for **1–3**. Photophysical characterization CV traces spectra for **1–3**. Supplementary computational output, including MO quantifications, ground and excited state dipole moment predictions. CCDC 922364 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50334h



All reactions were performed using standard Schlenk techniques under an inert (N₂) atmosphere, save for the Click reactions. Flash column chromatography was performed using silica gel (Silia-P from Silicycle, 60 Å, 40-63 µm). Analytical thin layer chromatography (TLC) was performed with silica plates with aluminum backings (250 µm with indicator F-254). Compounds were visualized under UV light. ¹H, ¹⁹F and ¹³C NMR spectra were recorded on a Varian INOVA spectrometer at 400 MHz, 376 MHz and 100 MHz respectively. The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "q" for quartet and "m" for multiplet. Perdeuterated acetonitrile (CD₃CN) or perdeuterated acetone (acetone- d_6) were used as the solvents of record. Spectra were referenced to the solvent peak and ¹⁹F spectra were referenced to trifluoroacetic acid (TFA). Exact mass measurements were performed on a quadrupole time-offlight (ESI-Q-TOF), model Maxis from Bruker in positive electrospray ionisation mode and spectra were recorded at the Université de Sherbrooke. 1,4-Bis(trimethylsilyl)butadiyne,⁸ azide,9 1-benzyl-4-phenyl-1*H*-1,2,3-triazole,¹ benzvl and 1-benzyl-4-(2,4-difluorophenyl)-1*H*-1,2,3-triazole¹ were synthesized following a literature procedure and the characterization matches that found in the literature. UV-vis and NMR-based photolysis studies were conducted in a photolysis reactor Rayonet (model RPR-200) using 16 × 35 W excitation lamps ($\lambda_{\text{exc}} = 300 \text{ nm}$).

4,4'-Bi-1H-1,2,3-triazole, 1,1'-bis(phenylmethyl), btl

To 1,4-bis-(trimethylsilyl)-1,3-butadiyne (800 mg, 4.11 mmol, 1.0 equiv.) in 1:1 isopropanol-water (80 mL) were added $CuSO_4 \cdot 5H_2O$ (467 mg, 1.87 mmol, 0.45 equiv.), K_2CO_3 (2.53 g, 23.6 mmol, 6 equiv.), ascorbic acid (701 mg, 4.0 mmol, 0.95 equiv.), benzyl azide (410 mg, 6.3 mmol, 1.5 equiv.) and pyridine (1.6 mL, 19.8 mmol, 5 equiv.). The mixture was placed under a N₂ atmosphere and then stirred for 24 h at room temperature. To the mixture was added 50 mL of dichloromethane and 50 mL of 28% aqueous NH₄OH. The organic layer was separated and then dried over Na₂SO₄, filtered and the solvent

evaporated under reduced pressure to yield the product as a white solid.

White solid. Yield: 64%. $R_{\rm f}$: 0.25 (DCM–acetone 95/5; silica). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 7.83 (s, 2H), 7.14–7.27 (m, 10H), 5.45 (s, 4H). ¹³C NMR (100 MHz, acetone-d₆) δ (ppm): 141.2, 137.1, 129.8, 129.2, 129.0, 121.8, 54.4. HRMS (ES-Q-TOF) (C₁₈H₁₆N₆Na⁺) Calculated: 339.1334; Experimental: 339.1332.

General procedure for formation of iridium(m) complexes

C^N ligand (2.20 equiv.) was mixed with IrCl₃·6H₂O (1.00 equiv.) in a mixture of 2-ethoxyethanol and water (6/1) to reach a concentration in IrCl₃·6H₂O of 0.04 M. The mixture was degassed by multiple vacuum and N₂ purging cycles. The suspension was heated at 130 °C for 24 h. A yellow precipitate formed and was collected by filtration and used without further purification. To this solid was added the btl ligand (1.10 equiv.) and 2-ethoxyethanol was added to reach a concentration in iridium of 0.04 M. The mixture was degassed by multiple vacuum and N₂ purging cycles. The suspension was heated at 130 °C for 24 h. The reaction mixture was cooled to room temperature and diluted with water. The aqueous suspension was washed several times with Et₂O. The aqueous layer was heated at 70 °C for 15 min and cooled back down to room temperature. A solution of NH₄PF₆ (10 equiv., 1.0 g/ 10 mL) was added dropwise to the aqueous phase to cause the precipitation of a yellow solid. The suspension was cooled to 0 °C for 1 h, filtered and the resulting solid was washed with cold water. The crude solid was purified by flash chromatography on silica gel using DCM to DCM-acetone (9/1).

Iridium(III) bis[2-phenylpyridinato-*N*,*C*²]-4,4'-bi-1*H*-1,2,3-triazole, 1,1'-bis(phenylmethyl) hexafluorophosphate (1)

Yellow solid. Yield: 15%. $R_{\rm f}$: 0.3 (DCM-acetone 9/1; silica). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 8.28 (s, 2H), 8.05 (d, J = 7.2 Hz, 2H), 7.88 (td, J = 7.2, 2.8 Hz, 2H), 7.71 (td, J = 8.0, 1.2 Hz, 4H), 7.35–7.40 (m, 4H), 7.18 (m, 2H), 7.07 (td, J = 5.6, 1.2 Hz, 2H), 6.96 (td, J = 8.0, 1.2 Hz, 4H), 6.82 (td, J = 8.0, 2.8 Hz, 4H), 6.26 (d, J = 8.0 Hz, 2H), 5.55 (s, 4H). ¹³C NMR (100 MHz, acetone-d₆) δ (ppm): 169.1, 150.4, 147.6, 145.6, 141.5, 139.5, 135.2, 132.8, 130.5, 130.1, 129.9, 129.1, 125.3, 124.6, 124.1, 123.0, 120.5, 56.1. ¹⁹F NMR (376 MHz, acetone-d₆) δ (ppm): -72.4 (d, J = 707 Hz, 6F). HRMS (ES-Q-TOF) (C₄₀H₃₂N₈Ir⁺) Calculated: 817.2379; Experimental: 817.2387.

Iridium(\mathfrak{m}) bis[(1'-phenyl)1,2,3-triazolato- $N, C^{2'}$]-4,4'-bi-1H-1,2,3-triazole, 1,1'-bis(phenylmethyl) hexafluorophosphate (2)

White solid. Yield: 35%. R_f : 0.3 (DCM-acetone 9/1; silica). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 8.32 (s, 2H), 8.12 (s, 2H), 7.44 (dd, J = 7.6, 1.2 Hz, 2H), 7.37–7.40 (m, 12H), 7.25 (td, J = 5.2, 2.4 Hz, 4H), 7.18 (td, J = 5.2, 2.4 Hz, 4H), 6.90 (td, J = 7.6, 1.2 Hz, 2H), 6.73 (td, J = 7.6, 1.2 Hz, 2H), 6.18 (d, J = 7.6, 2H), 5.58 (d, J = 4.0 Hz, 4H), 5.52 (s, 4H). ¹³C NMR (100 MHz, CD₃CN) δ (ppm): 158.0, 142.7, 141.7, 136.9, 135.4, 135.1, 133.7, 130.0, 129.9, 129.8, 128.8, 128.6, 128.4, 123.6, 123.4, 123.0, 120.6, 118.2, 56.2, 55.9. ¹⁹F NMR (376 MHz, acetone-d₆)

δ (ppm): -72.2 (d, J = 707 Hz, 6F). HRMS (ES-Q-TOF) (C₄₈H₄₀N₁₂Ir⁺) Calculated: 977.3128; Experimental: 977.3108.

$$\label{eq:relation} \begin{split} \mbox{Iridium(m)} bis[1'-(4',6'-diffuorophenyl)1,2,3-triazolato-N,C^{2'}]- \\ 4,4'-bi-1H-1,2,3-triazole, 1,1'-bis(phenylmethyl) \\ hexafluorophosphate (3) \end{split}$$

White solid. Yield: 36%. $R_{\rm f}$: 0.3 (DCM–acetone 85/15; silica). ¹H NMR (400 MHz, CD₃CN) δ (ppm): 8.31 (s, 2H), 8.16 (d, J = 1.6, 2H), 7.16–7.38 (m, 20H), 6.59 (td, J = 9.2, 2.0 Hz, 2H), 5.71 (dd, J = 8.8, 2.4 Hz, 2H), 5.58 (d, J = 2.8, 4H), 5.51 (d, J = 1.2, 4H). ¹⁹F NMR (376 MHz, acetone-d₆) δ (ppm): –72.3 (d, J = 707 Hz, 6F), –110.9 (q, J = 9 Hz, 2F), –113.2 (t, J = 10 Hz, 2F). HR-MS (ES-Q-TOF) (C₄₈H₃₆F₄N₁₂Ir⁺) Calculated: 1049.2749; Experimental: 1049.2737. Due to the low solubility of the product, we were unable to obtain a ¹³C NMR spectrum of sufficient resolution.

Photophysical measurements

All samples were prepared in either HPLC grade acetonitrile (ACN) or distilled 2-methyltetrahydrofuran (2-MeTHF), with concentrations on the order of 25 µM. Absorption spectra were recorded at room temperature in a 1.0 cm capped quartz cuvette, using a Shimadzu UV-1800 double beam spectrophotometer. Molar absorptivity determination was verified by a linear least squares fit of values obtained from at least three independent solutions at varying concentrations with absorptions ranging from 0.01 to 0.5 a.u. Steady-state emission spectra were obtained by exciting at the longest wavelength absorption maxima using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer equipped with double monochromators and a photomultiplier tube detector (Hamamatsu model R955). Emission quantum yields were determined using the optically dilute method.¹⁰ A stock solution for each complex with an absorbance of ca. 0.5 was prepared and then four dilutions were obtained with different dilution factors resulting in optical dilution absorbances of ca. 0.05-0.2. The Beer-Lambert law was assumed to remain linear at the concentrations of the solutions. The emission spectra were then measured after the solutions were rigorously degassed with solvent-saturated nitrogen gas (N2) for 10 minutes prior to spectrum acquisition using septa-sealed quartz cells from Starna. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor (R^2) for the linear fit of the dataset surpassed 0.98. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope obtained from the linear fit of these results. The equation $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$ was used to calculate the relative quantum yield of the sample, where $\Phi_{\rm r}$ is the absolute quantum yield of the reference, n is the refractive index of the solvent, A is the absorbance at the excitation wavelength, and I is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. A solution of [Ru(bpy)₃](PF₆)₂ in ACN $(\Phi_{\rm r} = 0.095)^{11}$ was used as the external reference. The

experimental uncertainty in the emission quantum yields is conservatively estimated to be 10%, though we have found that statistically we can reproduce PLQYs to 3% relative error.

Time-resolved excited-state lifetime measurements were performed using the time-correlated single photon counting (TCSPC) option of the Jobin Yvon Fluorolog-3 spectrofluorometer. A pulsed NanoLED at 341 nm (pulse duration <1 ns; fwhm = 14 nm), mounted directly on the sample chamber at 90° to the emission monochromator, was used to excite the samples and photons were collected using a FluoroHub single-photon-counting detector from Horiba Jobin Yvon. The lumine-scence lifetimes were obtained using the commercially available Horiba Jobin Yvon Decay Analysis Software version 6.4.1, included within the spectrofluorimeter. Lifetimes were determined through an assessment of the goodness of its mono-exponential fit by minimizing the chi-squared function (χ^2) and by visual inspection of the weighted residuals.

Electrochemistry

Cyclic voltammetry (CV) analyses were performed on an Electrochemical Analyzer potentiostat model 600D from CH Instruments. Solutions for cyclic voltammetry were prepared in distilled ACN and degassed with ACN-saturated nitrogen bubbling for *ca.* 15 min prior to scanning. Tetra(*n*-butyl)-ammonium hexafluorophosphate (TBAPF₆; *ca.* 0.1 M in ACN) was used as the supporting electrolyte. A non-aqueous Ag/Ag⁺ electrode (silver wire in a solution of 0.1 M AgNO₃ in ACN) 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. The redox potentials are reported relative to a saturated calomel electrode (SCE) with a ferrocenium/ferrocene (Fc⁺/Fc) redox couple as an internal reference (0.38 V *vs.* SCE).¹²

Computations

Density functional theory (DFT) calculations. All calculations were performed with the Gaussian 0913 suite. The level of theory for all DFT¹⁴ and TD-DFT¹⁵ calculations was B3LYP; excited-state triplet geometries were calculated using the unrestricted B3LYP method (UB3LYP).¹⁶ The 6-31G* basis set¹⁷ was used for C, H and N directly linked to iridium while the other C, H, N and F atoms were undertaken with the 3-21G* basis set,¹⁸ and the VDZ (valence double ζ) with SBKJC effective core potential basis set18a,19 was used for iridium. The X-ray structure of 3 was used as the input geometry for the S₀ optimization calculation for 3 and the structure modified accordingly for 1 and 2. Frequency calculations performed on each optimized structure resulted in only positive vibrational frequencies. The predicted phosphorescence wavelengths were obtained by energy differences between the triplet and singlet optimized states at their respective optimized geometries $(E_{0,0})^{20}$ and also as the energy difference between the triplet and singlet optimized states at the optimized geometry of the triplet state (E_{AE}). The energy, oscillator strength and related MO contributions for the 100 lowest singlet-singlet and 5 lowest singlet-triplet excitations were obtained from the

TD-DFT/singlets and the TD-DFT/triplets output files, respectively. The calculated absorption spectra were visualized with GaussSum 2.1 (fwhm: 1000 cm⁻¹).²¹ An ACN quantum mechanical continuum solvation model as implemented within Gaussian 09 was employed.²²

Results and discussion

Ligand and complex synthesis

The 1,1'-dibenzyl-4,4'-bi-1H-1,2,3-triazolyl (btl) ligand was obtained in 64% yield through a tandem silyl-deprotection and Cu^I-catalyzed azide–alkyne cycloaddition reaction between benzyl azide and 1,4-bis(trimethylsilyl)butadiyne, itself obtained via a Glaser-type coupling reaction (Scheme 1), similar to a protocol reported by Fletcher and co-workers.^{6c} All the complexes were synthesized through cleavage of the respective µ-dichloro-bridged iridium(III) dimers with 2.22 equivalents of btl in refluxing 2-ethoxyethanol.23 Following anion metathesis of the chloride salt with NH₄PF₆, pure complexes were obtained as their hexafluorophosphate salts. Complex 1 is a pale yellow solid while 2 and 3 are white solids. Each complex was purified on silica gel and satisfactory microanalysis was obtained for each. Additionally and fortuitously, we were able to grow single crystals of sufficient quality of 3 for the structure to be solved by X-ray single crystal diffraction analysis.

Crystal structure

Single crystals of sufficient quality of **3** were grown from a mixed solution of chloroform and diisopropyl ether by slow diffusion. Complex **3** crystallizes in the triclinic space group $P\bar{1}$ as a racemic mixture with one molecule (Λ -isomer) in the asymmetric unit with the Δ -isomer related to the Λ -isomer *via* the crystallographic inversion center. The structure of the Λ -isomer is shown in Fig. **1**. The structure additionally contains two chloroform solvate molecules. The [PF₆]⁻ anion is disordered over two sites in a 65:35 ratio with the two orientations related *via* rotation about one of the molecular 4-fold axes with the axial F atoms weakly hydrogen bonded to one of the CHCl₃ solvate molecules. In addition there are numerous short CH-triazole…F_{anion} contacts in **3** though the disorder in the anion position would indicate that either of these



Scheme 1 Synthesis of the btl ligand and complexes 1-3



Fig. 1 ORTEP diagram at 30% probability of the [(dFphtl)₂Ir(btl)]⁺ cation of **3** (unit cell parameters: *a* 12.729(2) Å; *b* 15.350(3) Å; *c* 15.924(3) Å; *a* 116.212(4)°; β 93.122(4)°; γ 98.548(5)°). Counterions, solvent molecules and hydrogen atoms have been removed for clarity. Selected bond parameters: Ir–C_{dFphtl} = 2.020(5), 2.028(5); Ir–N_{dFphtl} = 2.009(5), 2.030(5); Ir–N_{btl} = 2.152(5), 2.156(4) Å; C_{dFphtl}–Ir–N_{dFphtl} = 80.2(2), 80.3(2); N_{btl}–Ir–N_{btl} = 75.99(17); (N–C–C–N)_{btl} = 0.7(8)°.

interactions are not structure directing (or at least two conformations are near equi-energetic).

The structure of 3 adopts a distorted octahedral coordination environment (Fig. 1). The coordinating nitrogen atoms of the dFphtl ligands are disposed in a mutually trans configuration while the cyclometallating carbon atoms are found trans to the datively bound nitrogen atoms of the btl ligand. The benzyl groups of the dFPhtl ligands are rotated away from the btl while the benzyl groups of the latter ligand adopt a mutually anti conformation. The bite angles about iridium are very similar to those of [(bpy)2Ru(btl)]Cl2 [(N-Ru-N)btl = 77.68(10)°],^{6b} and the average C_{dFphtl}-Ir-N_{dFphtl} bond angle in 6 (79.6°).^{3a} No twisting of the central C–C bond of the btl unit is observed in 3. The bond lengths found in 3 are very similar to the average bond lengths in the crystals structure of 6 $(Ir-C_{dFphtl} = 2.027, Ir-N_{dFPhtl} = 1.988 \text{ and } Ir-N_{bpy} = 2.129 \text{ Å}; the$ longer Ir-N_{btl} bonds suggest a weaker coordination of the ancillary ligand in 3 than in 6.

Electrochemical characterization

The ground state electronics of 1–3 were probed through electrochemical studies by means of cyclic voltammetry (CV) and are shown in Fig. 2. The CV data are summarized in Table 1. All oxidation and reduction waves are irreversible. The oxidation waves of both 1 and 2 are essentially identical at *ca.* 1.27 V and similar to that found for $[(ppy)_2Ir(bpy)]$, 4 and $[(pht)_2Ir(bpy)]$, 5 ($E_{pa}^{OX} = 1.28$ V for 4 and 1.29 V for 5).^{3a} Thus, as with 4 and 5, replacement of the ppy ligands with phtl does not influence the stability of the HOMO. The increased irreversibility of the oxidation wave points to an increased contribution from the C^N ligands to the mixed oxidation, which also implicates an Ir^{III}/Ir^{IV} redox couple. The oxidation in 3 is shifted anodically by 370 mV compared to 2 due to the presence of the electron-withdrawing fluorine atoms on the dFphtl

C^N ligands, similar to that observed for [(dFphtl)₂Ir(bpy)], 6 $(E_{\text{pa}}^{\text{Ox.}} = 1.64 \text{ V})$. The first reduction waves in 2 and 3 are separated by only 30 mV and are assigned to the reduction of the btl ligand, the reduction of 3 also modestly influenced by the fluorine atoms on the C^N ligands. Analogously, the second reduction in 1 is assigned to reduction of the btl. The first reduction event in 1 at -1.99 V is 280 mV less negative than 2 and corresponds to the addition of an electron to the ppy ligands.²⁴ The electrochemical gap increases from 3.25 through to 3.88 V from 1 through 3, which are all substantially larger than that found for sky-blue emitter 6 ($\Delta E_{redox} = 3.09 \text{ V}$) and sandwich the ΔE_{redox} = 3.68 V measured for deep blue emitter Ir(4-(t-butyl)-2',6'-difluoro-2,3'-bipyridine)2(1,10dimethyl-3,3'-methylenediimidazolium carbene), recently reported by Baranoff and co-workers.²⁵ The trends observed in the CV traces and assignments are corroborated in their entirety by DFT calculations (vide infra).

Photophysical characterization

The absorption spectra for **1–3** in ACN show similar features (Fig. 3). There is a progressive blue shift in the absorption spectra from **1–3**, which mirrors the increasing electrochemical gap observed in the CV studies. The high intensity absorption bands above 250 nm are assigned to ligand-based $\pi \rightarrow \pi^*$ transitions while the low intensity bands beyond 300 nm are mixed charge-transfer (CT) transition involving both metal-to-ligand (¹MLCT), intra-ligand (¹ILCT) and ligand-to-ligand



Fig. 2 CV traces for **1–3** in deaerated ACN with 0.1 M nBu_4PF_6 as the supporting electrolyte at 298 K. $\nu = 0.1$ V s⁻¹.

(¹LL'CT) charge transfers. From the time-dependent DFT (TDDFT) calculations (*vide infra*), these CT transitions in $\mathbf{1}$ are mixed with LC transitions as well.

The photoluminescent emission spectra at 298 K in ACN solutions and at 77 K in 2-MeTHF rigid glass matrixes are also shown in Fig. 3 and the photophysical data are summarized in Table 2. The 298 K emission in 1 is somewhat structured with a high-energy shoulder at 481 nm and a maximum at 511 nm. This structured emission, combined with the absence of a rigidochromic shift upon cooling to 77 K, is indicative of emission with strong LC character. The 298 K emission centred at 495 nm in 2 is unstructured, which implies a strong CT character to the emission. Upon cooling, there is a rigidochromic shift of 4368 cm^{-1} and the 77 K emission spectrum, as with 1, becomes structured. The 77 K emission spectrum of 5 by contrast remains unstructured. Thus, due to the use of the more electron-rich btl ligand, the energy of the LUMOs increases and results in increased LC character to the emission. The assignments of the nature of the emission for 1 and 2 are supported by theoretical calculations (vide infra). The emission maxima for 1 and 2 are each significantly blueshifted compared to 4 (λ_{em} = 602 nm) and 5 (λ_{em} = 580 nm). Complex 1 in fact shows a similar photophysical profile to $[Ir(ppy)_2(phpzpy)]PF_6 (\lambda_{em} = 480 \text{ nm}, \Phi_{PL} = 3\%, \tau_e = 0.18 \text{ }\mu\text{s}),$ where phpzpy = 2-(1-phenyl-1*H*-pyrazol-3-yl)pyridine.²⁷ Unfortunately, 3 was found to not be photostable at ambient



Fig. 3 Absorption in ACN solution at 298 K, emission in ACN at 298 K and emission in 2-MeTHF at 77 K for $1\!-\!3$.

Table 1 Electrochemical data of 1–3 ^a									
Complex	$E_{\rm pa}^{\rm Ox.}$	$E_{\rm pc}^{\rm Red.}$ 1	$E_{\rm pc}^{\rm Red.}$ 2	$E_{\rm pc}^{\rm Red.}{}_3$	$E_{\rm HOMO}^{\ b}/{\rm eV}$	$E_{\rm LUMO}$ ^b /eV	$\Delta E_{ m redox}$ ^c		
1	1.26	-1.99	-2.23	-2.41	-6.06	-2.79	3.25		
2	1.27	-2.27	_	_	-6.07	-2.53	3.54		
3	1.64	-2.24	-2.43	—	-6.44	-2.56	3.88		

^{*a*} Measured in N₂-saturated ACN (*ca.* 1.5 mM) with *n*Bu₄NPF₆ (*ca.* 0.1 M), 298 K, glassy carbon 3 mm as the working electrode, $\nu = 0.05$ V s⁻¹. Potentials are reported in V *versus* SCE and were calibrated with an internal standard Fc/Fc+ redox couple (0.38 V *vs.* SCE in ACN).¹² E_{pa} = anodic potential. E_{pc} = cathodic potential. ^{*b*} The HOMO and LUMO energies were calculated using the relation $E_{HOMO/LUMO} = -(E_{onset Ox./Red. vs. Fc} + 4.8)$ eV.^{26 c} $\Delta E_{redox} = E_{pa}^{coc} - E_{pc}^{red}$.

 Table 2
 Spectroscopic and photophysical data for 1–3^a

		$\lambda_{\rm em}/{\rm nm}$			$ au_{ m e}/\mu{ m s}$			
	$\lambda_{abs}\left(\varepsilon\right)/nm\left(\times10^{3}\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1} ight)$	298 K	77 K	${\Phi_{ m PL}}^{b}$ /%	298 K	77 K	$k_{\rm r}/\times 10^5 {\rm \ s}^{-1}$	$k_{\rm nr} / \times 10^5 \ {\rm s}^{-1}$
1 2 3	252 (45.5); 330 (8.55); 375 (4.50) 229 (65.5); 300 (8.16) 226 (20.8); 294 (8.80)	481 (0.86); 511 (1.0) 495 c	470 (1.0); 506 (0.88) 407 (1.0); 434 (0.79) 393 (1.0); 419 (0.84)	2.8 2.7	$2.17 \\ 4.77 \times 10^{-2}$	4.77 15.8	0.129 5.66	4.48 204

^{*a*} Measurements at 298 K in ACN and at 77 K in the 2-MeTHF glass state. Absorption measurements in aerated solution and 298 K emission measurements in N₂-saturated solution. Relative intensities of structured emission spectra in parentheses. ^{*b*} Measured using [Ru(bpy)₃]PF₆ ($\Phi_{PL} = 9.5\%$ in ACN) as the reference.^{11 c} Complex not photostable. See text.

temperature (*vide infra*) but did exhibit structured emission at 77 K that is further blue-shifted compared to **2**.

Photoluminescent quantum yields for **1** and **2** were modest at ~3%. However, their excited-state decay kinetics are quite distinct. Compound **1** shows microsecond 298 K lifetimes that are approximately doubled at 77 K. By contrast, the 298 K τ_e for **2** is only 48 ns while the emission is very long-lived at 15.8 µs and 77 K. This translates to a 44 fold increase in the radiative rate constant, k_r , offset by a 46 fold increase in the non-radiative rate constant, k_{nr} .

Photodecomposition studies of 3

Upon excitation of a dilute ACN solution of single crystals of **3** at 290 nm (concentrations below 1 μ M), we observed unusual behaviour in the emission spectrum with maxima at 352 and 505 nm. Over successive scans, the peak at 505 nm decreased in intensity (Fig. 4a). LC-HRMS analysis of an aliquot after 20 scans revealed several unidentified decomposition products, including two solvento iridium complexes as the major products, [Ir(dFphtl)₂(ACN)₂]⁺ and [Ir(dFphtl)₂(ACN)(S)]⁺, where S is another weakly bound solvent molecule.

In order to investigate the nature of this decomposition, we conducted photolysis experiments of 3 (λ_{exc} = 300 nm, Rayonet photochemical reaction model RPR-200 operating with 16 lamps of 35 W) over 20 min. Decomposition progression was monitored firstly by UV-vis absorption at µM concentrations (Fig. 4b). An isosbestic point at ca. 210 nm was observed with the ¹LC absorption band at 229 nm decreasing in intensity. The ¹CT band at 296 nm also decreases in intensity and shifts hypsochromically over the course of irradiation. Finally, in a subsequent experiment, decomposition of 3 was monitored by ¹H NMR in CD₃CN at mM concentrations (Fig. 4c). Signals characteristic of the btl in 3, such as the singlet at 8.33 ppm associated with the proton of the triazole, disappear during the photolysis, suggesting decomplexation and subsequent degradation of the btl ligand. The proton of the triazole fragment of the dFphtl ligands at 8.19 ppm disappears and is replaced by a singlet at 8.15 ppm. A similar analysis can be made for the benzylic protons wherein the doublet of doublets at 5.73 and the doublet at 5.54 ppm disappear over the course of the photolysis while the doublet at 5.61 ppm converges into a singlet. These characteristic ¹H NMR signals are reminiscent of those found for N,N-trans-[Ir(dFphtl)₂(CD₃CN)Cl] (¹H NMR in CD₃CN), reported by Fernández-Hernández and co-



Fig. 4 Evidence of photodecomposition of **3**. (a) Emission spectra obtained in deaerated sub- μ M ACN solution at 298 K (λ_{exc} = 290 nm); (b) absorption spectra obtained in aerated μ M ACN solution during photolysis experiments (see text); (c) ¹H NMR spectra in mM CD₃CN solution during photolysis experiments (see text).

workers.^{3d} LC-HRMS analysis conducted after 20 min irradiation revealed several unassigned low molecular weight decomposition products along with the previously detected $[Ir(dFpht]_2(ACN)_2]^+$ and $[Ir(dFpht]_2(ACN)(S)]^+$. From these experiments we can conclude that the energy required to excite **3** also promotes a dissociation and decomposition of the btl ligand, with acetonitrile solvent molecules coordinating the vacant sites about iridium. This decomposition pathway is distinct from the more commonly observed one in blue-emitting iridium complexes, which involves photochemical cleavage of one of the two $Ir-N_{C^N}$ bonds, necessitating a geometric change and thus thermally accessing a metal-centered (³MC) state.²⁸ This non-emissive state is then prone to subsequent adventitious attack by a small molecule.²⁹

DFT computations

A detailed density functional theory (DFT) and time-dependent DFT (TDDFT) study was undertaken to model the optoelectronic properties of 1-3. We have previously shown that a similar computational methodology incorporating the SBKJC-VDZ basis set on iridium accurately predicts both ground- and excited-state properties for triazole-containing iridium complexes.^{3a,g} In order to assess the quality of the predictions, we contrasted the computed ground state structures of 1-3 with those, respectively, of the reference X-ray structures for 4-6 along with the X-ray structure of 3 obtained in this study. An analysis of Table 3 reveals a good accord between the predicted geometries and those from the X-ray structures. Computed Ir-C_{C^N} and Ir-N_{C^N} bond lengths are overestimated by less than 3%. Replacement of a bpy ligand with a btl results in a slight elongation of the computed Ir– $N_{N^{\wedge}N}$ bond of 0.069, 0.064, 0.048 Å, respectively in 1 versus 4, 2 versus 5 and 3 *versus* 6; the predicted Ir- $N_{N^{\wedge}N}$ bond length in 3 overestimates the average bond lengths in the crystal structure by only 0.3%. The computations thus reproduce the weaker coordination of the btl compared to bpy. The bite angle for the btl is comparable to that of bpy. The computations also accurately predict the $C_{C^{n}}$ -Ir- $N_{C^{n}}$ bond angle. The geometry in the triplet state remains essentially unchanged compared to that in the ground state. Therefore, we believe that the agreement between computed geometries and those of the crystal structures of the reference complexes 4-6, along with a more direct comparison with 3, is sufficient to ensure a proper description of their optoelectronic properties.

Fig. 5 shows compiled Kohn-Sham energy diagrams of the five highest-energy occupied and the five lowest-energy unoccupied molecular orbitals (MOs) for 1-3 along with electron density contour plots of selected MOs. Quantification of the localization of the electron density within each of these MOs along with their relative energies are shown in Fig. S7–S9[†] for 1–3, respectively. For each of the complexes, the HOMO is distributed on the iridium and the C^N ligands with decreasing iridium contribution from 43% to 39% to 32% along the series. The HOMO - 1 is localized almost exclusively on the C^N ligands for all three complexes. For 1, the electron density in HOMO - 2 to HOMO - 4 is shared between the Ir and C^N. The HOMO - 2 and HOMO - 3 for 2 and the HOMO - 2 and HOMO - 4 for 3 possess topologies with significant C^N contributions. The HOMO - 4 in 2 and the HOMO - 3 in 3 include contributions from the btl of 18 and 32%, respectively. The LUMO for 1 is localized exclusively (94%) on the ppy while for 2 and 3 it is mainly (75%) on the btl. The LUMO + 1 for all three complexes is located in the C^N ligand. The LUMO + 2 in 1 is mainly localized on the btl while in 2 and 3 it is localized on the C^N ligands.

Replacement of ppy with phtl destabilizes the LUMO in 2, resulting in a 0.41 eV increase in the HOMO-LUMO gap compared to 1. Addition of fluorine atoms onto the C^N ligands in 3 promotes stabilization of both the HOMO and LUMO. The stabilization is more pronounced for the occupied MOs resulting in a 0.24 eV increase in the HOMO-LUMO gap from 2 to 3. While the HOMO is relatively isolated from the other lowerenergy occupied MOs, the same is not the case for the LUMO. For 1, the LUMO + 1 is very close in energy to the LUMO and is destabilized by only 0.07 eV. For 2, LUMO + 1 through LUMO + 3 are essentially electronically degenerate and are only 0.19 eV higher in energy than the LUMO. Similarly observed for 3, these same MOs are separated by only 0.06 eV with the LUMO + 1 destabilized by 0.15 eV compared to the LUMO. The phtl and dFphtl ligands possess higher energy π^* orbitals than ppy, permitting less mixing in the excited state and conserving greater CT character in the emission.

We have calculated the 100 lowest-energy vertical singletsinglet and 5 lowest-energy singlet-triplet transitions using TDDFT to permit assignment of the nature of the different absorption bands and to provide insight into the nature of the emission. The most important low energy vertical transitions are summarized in Table 4. Unlike the case found in most

Table 3 Selected computed S ₀ geometric parameters, bond lengths in Å and bond angles in deg (°), for 1–3 ^a								
	1	4^{b}	2	5 ^{<i>c</i>}	3	3^d	6 ^{<i>c</i>}	
(Ir-C _{C^N}) _{avg}	2.022	2.014	2.045	2.010	2.045	2.024	2.027	
(Ir-N _{C^N}) _{avg}	2.076	2.045	2.042	1.994	2.049	2.020	1.988	
(Ir-N _{N^N})avg	2.202	2.133	2.192	2.128	2.177	2.154	2.129	
$(C_{C^{N}}-Ir-N_{C^{N}})_{avg}$	80.4	80.4	79.9	78.3	80.4	80.3	79.6	
N _{N^N} -Ir-N _{N^N}	74.8	76.2	75.3	76.3	75.5	76.0	77.0	

^{*a*} Average distances and angles reported. ^{*b*} Data from ref. 30. ^{*c*} Data from ref. 3*a*. ^{*d*} Data taken from the Λ isomer found in the crystal structure (*vide supra*).



Fig. 5 Calculated energy level scheme for the Kohn–Sham orbitals between HOMO – 4 to LUMO + 4 for 1–3, including contour plots (0.02 isovalue) of selected most relevant MOs and the associated DFT calculated HOMO–LUMO energy gap (in eV).

Table 4	Principal theoretical low energy singlet-singlet and singlet-triplet electronic transitions with corresponding oscillator strengths (f) and assign	ments fc	٥r
1–3 ^a			

				Energ	у	Occillator strongth	
	State	Nature of transition (contribution in %)	Primary character	(eV)	(nm)	(f)	
1	$\begin{array}{c} S_1\\S_5\\S_7\\S_9\\T_1\\T_2 \end{array}$	$\begin{array}{l} \text{HOMO} \rightarrow \text{LUMO (98\%)} \\ \text{HOMO} \rightarrow \text{L} + 4 (92\%) \\ \text{H} - 4 \rightarrow \text{LUMO (10\%)}, \text{H} - 2 \rightarrow \text{LUMO (71\%)} \\ \text{H} - 2 \rightarrow \text{LUMO (14\%)}, \text{H} - 1 \rightarrow \text{L} + 1 (74\%) \\ \text{H} - 1 \rightarrow \text{L} + 1 (18\%), \text{HOMO} \rightarrow \text{LUMO (63\%)} \\ \text{H} - 1 \rightarrow \text{LUMO (26\%)}, \text{HOMO} \rightarrow \text{L} + 1 (53\%) \end{array}$	$\begin{array}{l} MLCT_{ppy}/LC_{ppy}/ILCT_{ppy}\\ ML'CT/LL'CT/ILCT_{ppy}\\ MLCT_{ppy}/LC_{ppy}/ILCT_{ppy}\\ LC_{ppy}\\ LC_{ppy}/MLCT_{ppy}/ILCT_{ppy}\\ LC_{ppy}/MLCT_{ppy}/ILCT_{ppy}\\ \end{array}$	3.25 3.88 3.98 4.04 2.88 2.92	382 320 312 307 431 425	0.1128 0.0442 0.0653 0.1246 0 0	
2	$S_1 \\ S_5 \\ S_8 \\ S10 \\ T_1 \\ T_2$	$\begin{array}{l} \text{HOMO} \rightarrow \text{LUMO (94\%)} \\ \text{HOMO} \rightarrow \text{L} + 4 \ (45\%), \ \text{HOMO} \rightarrow \text{L} + 5 \ (48\%) \\ \text{H} - 1 \rightarrow \text{LUMO (86\%)} \\ \text{H} - 1 \rightarrow \text{L} + 1 \ (77\%) \\ \text{H} - 1 \rightarrow \text{L} + 6 \ (17\%), \ \text{HOMO} \rightarrow \text{L} + 1 \ (12\%), \ \text{HOMO} \rightarrow \text{L} + 5 \ (21\%) \\ \text{H} - 1 \rightarrow \text{L} + 5 \ (21\%), \ \text{HOMO} \rightarrow \text{L} + 1 \ (12\%), \ \text{HOMO} \rightarrow \text{L} + 6 \ (22\%) \end{array}$	MLCT _{btl} /LL'CT LC _{phtl} /MLCT _{btl} /LL'CT MLCT _{phtl} /LL'CT MLCT _{phtl} /ILCT _{phtl} MLCT _{phtl} /LC _{phtl} MLCT _{phtl} /LC _{phtl}	3.69 4.14 4.31 4.45 3.32 3.34	336 299 288 279 374 371	0.0020 0.1351 0.0322 0.0486 0 0	
3	S_1 S_5 S_6 T_1 T_2	$\begin{array}{l} \text{HOMO} \rightarrow \text{LUMO (93\%)} \\ \text{H} - 1 \rightarrow \text{LUMO (91\%)} \\ \text{HOMO} \rightarrow \text{L} + 4 \ (47\%), \text{HOMO} \rightarrow \text{L} + 5 \ (42\%) \\ \text{H} - 1 \rightarrow \text{L} + 1 \ (14\%), \text{H} - 1 \rightarrow \text{L} + 6 \ (17\%), \text{HOMO} \rightarrow \text{L} + 2 \ (25\%), \\ \text{HOMO} \rightarrow \text{L} + 5 \ (16\%), \\ \text{H} - 1 \rightarrow \text{L} + 2 \ (16\%), \text{H} - 1 \rightarrow \text{L} + 5 \ (18\%), \text{HOMO} \rightarrow \text{L} + 1 \ (22\%), \\ \text{HOMO} \rightarrow \text{L} + 6 \ (18\%), \end{array}$	MLCT _{btl} /LL'CT MLCT _{btl} /LLCT MLCT/LL'CT/LC _{dFphtl} ILCT _{dFphtl} /LC _{dFphtl} / MLCT _{dFphtl} ILCT _{dFphtl} /LC _{dFphtl} / MLCT _{dFphtl}	3.94 4.36 4.42 3.39 3.41	315 284 281 366 364	0.0018 0.0344 0.1307 0	

 a H = HOMO; L = LUMO; MLCT = metal-to-ligand charge transfer; LL/CT = ligand-to-ligand charge transfer; ILCT = intra-ligand charge transfer; LC = ligand-centered. For the primary character, the order indicated reflects the predominance of the different transitions (threshold >10%).

cationic iridium complexes, the oscillator strength for the HOMO \rightarrow LUMO transition in **1** is large (f = 0.1128) and involves redistribution of the electron density about the ppy ligands. This transition is best described as possessing mixed charge-transfer (CT)/ligand-centered (LC) character. By contrast, the principal low-energy and low-intensity transitions for **2** and **3** are mixed metal-to-ligand/ligand-to-ligand MLCT/LL' CT and implicate the btl unit. The proportion of LC character

increases markedly for higher-energy transitions (λ_{abs} < 300 nm). Overall, the calculations reproduce the principal features of the experimental absorption spectra, however this comparison is rendered difficult due to the dearth of identifiable bands and structure.

For each complex, the T_1 and T_2 states reside within 0.04 eV of one another. Ascription of the nature of emission is difficult given the great number of distinct transitions required to



describe each excited state and it is a challenge to deconvolute the ratio of LC/CT character in the emission. However, for each of the complexes, these triplet states largely implicate the C^N ligands and the iridium but not the btl ligand, a behavior distinct from that calculated for 5 and 6.^{3a} Thus, based on the TDDFT analysis, emission in each involves a combination of LC_{C^N} , ILCT_{C^N} and MLCT_{C^N}. Complex 1 possesses the greatest amount of ³LC character while emissions for 2 and 3 possess significant ³CT character. These assignments are closely aligned with the experimental findings.

In order to obtain a better description of the nature of the lowest-energy triplet state, the geometry and energy of the T_1 state for each complex were fully optimized using unrestricted B3LYP (UB3LYP). The spin densities for each of 1–3 (Fig. 6) are localized on the iridium and one of the C^N ligands. From an analysis of the spin density distribution, the emission results from a mixed $LC_{C^N}/ILCT_{C^N}/MLCT_{C^N}$ state, corroborating the TDDFT calculations. Importantly, from these calculations the btl moiety is not involved in the emission. The calculations in concert with the experimental results suggest that in 1 the ³LC character is more pronounced than in 2 or 3.

The predicted emission energies were assessed using two approaches: Method 1 is the energy difference between the T_1 and So states at their respective optimized geometries and best reflects the $E_{0,0}$ band of the 77 K emission; Method 2 is an adiabatic energy difference between the T1 and S0 states at the optimized geometry of the T1 state and best reflects the emission energy at 298 K. The predicted emission energies employing method 1 ($E_{0,0}$) are 426, 403 and 413 nm while those employing method 2 (E_{AE}) are 468, 508 and 501 nm, respectively, for 1-3. While the predictions match very well with 2 $(\lambda_{em}(77 \text{ K}) = 407 \text{ nm}; \lambda_{em}(298 \text{ K}) = 495 \text{ nm})$, they are somewhat less reliable for 1 ($\lambda_{em}(77 \text{ K}) = 470 \text{ nm}; \lambda_{em}(298 \text{ K}) = 511 \text{ nm}); 3$ is photochemically unstable at 298 K but luminesces at low temperature (λ_{em} (77 K) = 393 nm) rendering a comparison within method 2 impossible (vide supra). The overestimation of the emission energy of 1 regardless of the method employed suggests that the calculations are underestimating the importance of the ³CT character to the mixed ³LC/³CT emission of 1. For each complex, the ground-state dipoles are oriented as to bifurcate the btl ligand (Fig. S10-S12⁺).

The excited-state dipole in **1** remains essentially unchanged compared to the ground state dipole. There is a slight decrease of 3.2 D in the magnitude of the excited state dipole in **2** while its orientation is not significantly impacted. By contrast, both the orientation and the magnitude of the excited state dipole in **3** are significantly perturbed with a calculated increase of 7.9 D.

Conclusion

In conclusion, a family of cationic iridium complexes incorporating a bis(triazole) ancillary ligand have been synthesized and their optoelectronic properties characterized. When the cyclometallating ligand is ppy, the experimental data and computations point to a mostly ligand-centered, blue-green emission. When the main ligands are based on an aryltriazole motif, the characterization and theoretical studies imply an emission with much greater charge-transfer character. With phtl as the C^N ligand, emission is sky-blue but very short-lived while with dFphtl the complex is not photostable at room temperature. Their photophysical properties coupled with electrochemical irreversibility thus do not render these complexes as prime candidates for incorporation into electroluminescent devices.

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