

Deep colour tuneability of heteroleptic Ir(III) complexes through second sphere coordination

Barbora Balónová, T. Harri Jones, Allison E. True, Sydney M. Hetherington and Barry A. Blight *

Department of Chemistry, University of New Brunswick, Fredericton, NB, E3B 5A3, Canada

* Corresponding author: b.blight@unb.ca

ABSTRACT:

Novel iridium (III) complexes with different systems of cyclo-metallating ligands bearing the general formula $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]$ were synthesized, characterized and their photophysical properties measured. Incorporation of guanidine moieties into iridium complexes allows us to introduce a hydrogen-bonding array for the formation of self-assembled iridium hydrogen-bonded systems. Through a series of UV-vis binding studies we demonstrated the host-guest chemistry of these systems display high levels of colour tuneability. The introduction of these hydrogen-bond modifications was also shown to have significant impacts on chromaticity, quantum yields and lifetimes with emphasis on energy transfer studies based on second-sphere coordination methodology.

KEYWORDS: H-Bonding, Colour tuning, Second-Sphere Interactions

Introduction

Iridium complexes have aroused significant research interest due to their various applications such as bioimaging,¹⁻³ organic photovoltaic cells,⁴⁻⁵ and catalysis.⁶⁻⁷ Particularly, the implementation of iridium complexes as emitters in phosphorescent organic light-emitting diodes (PhOLEDs) has attracted great attention.⁸ Cyclometallated iridium complexes have exhibited short lifetimes in excited states and high photoluminescence efficiencies which makes them particularly interesting when exploited in PhOLEDs.⁹⁻¹¹

Phosphorescent iridium emitters can harvest both the generated singlet and triplet excitations which theoretically makes them able to realize a 100 % internal quantum efficiency and gives them an advantage in comparison to fluorescent systems, which can only reach a maximum of 25 %.¹² To fulfil the requirements of full-colour OLED displays, the colour regulation toward efficient red, green and blue emissions is highly desirable. Colour tunability is one of the key features of cyclometallated iridium complexes,¹³⁻¹⁶ and can be achieved through synthetic modifications of C^N ligands by a delicate balance between energy of frontier orbitals which are taking part in the photoexcitation process.

The major triplet excited states observed in phosphorescent iridium complexes, according to Shakirova et al.,¹⁷ are (a) metal perturbed intra-ligand (³IL) transition (or ligand centred transition), (b) metal to ligands charge transfer (³MLCT) and (c) inter-ligand charge transfer (³LLCT). The energy of the excited states can be changed in multiple ways, but the most common approach is the synthetic modification of C^N ligands through incorporation of either donor or acceptor substituents.¹⁸⁻²¹ Other methodologies that can shift the emission colour of iridium complexes include size variations with increase of rigidity of the cyclometallating ligands, for instance, dibenzo[f,h]quinoxaline ligands that are able to bathochromically shift the phosphorescence colour.²²

To date, cyclometallated iridium complexes emitting in green and blue regions have reported high quantum efficiencies.²³ On the other hand, orange and red emitting iridium complexes typically suffer from lower quantum yields since the radiative rate constant (k_r) has a dependence on the excited state energy⁵ and it usually decreases with longer emission wavelengths.²⁴

Blue iridium complexes are still under investigation for their application in the display and lighting industry as they have still relatively low efficiencies compared to standard Ir(III) red and green devices. According to Pal *et al.*,²⁶ these are the criteria for deep blue emitters: i) process the required chromaticity standards defined by the National Television System Committee (NTSC) and European Broadcasting Union (EBU) with Commission International de l'Éclairage (CIE)²⁷ coordinates of (x=0.14, y=0.08) and (x=0.15, y=0.06), respectively; ii) possess high photoluminescence quantum yields (Φ_{PL}) that translate into high external quantum efficiencies in OLED and iii) exhibit competitive device stabilities to fluorescent complexes.²⁸

Despite the efforts of various research groups,²⁹⁻³⁰ the design and synthesis of stable, efficient and pure blue iridium complexes remains challenging. This study presents the design and synthesis of neutral iridium complex **1** (Figure 1), with cyan-blue emission in CHCl₃ solution with CIE coordinates: x=0.18, y=0.31. The chromaticity of complex **1** can be modified and reach deep blue emission (CIE coordinates: x=0.15, y=0.11) when combined with compound **5** (Figure 2). Furthermore, we prepared neutral yellow complex **2** and red/orange emissive iridium complexes **3** and **4** (Figure 1), which are also desirable for their application in the display industry, but moreover the iridium complexes with red emission are often exploited in bioimaging and anticancer studies.³¹⁻³² The reasoning behind the synthesis of yellow complex **2** was to examine if white emission can be achieved by combining it with guest **5** (blue

fluorescence in solution), as white emission is a crucial component in white OLEDs (WOLEDs).³³⁻³⁴

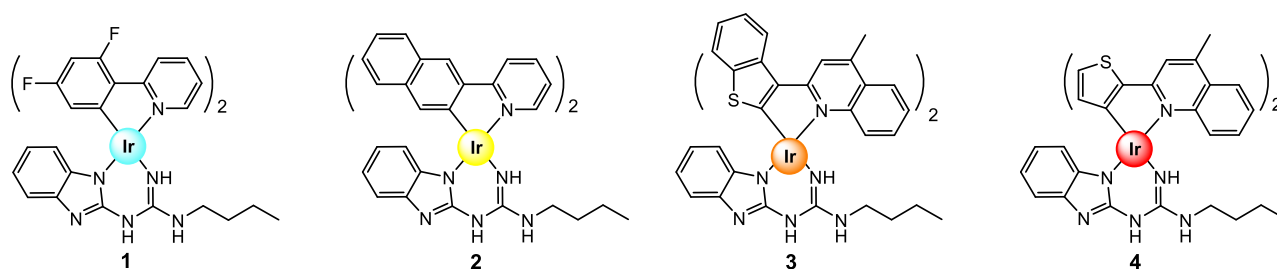


Figure 1. Cyclometallated Ir(III) complexes **1-4** studied herein.

Usually, WOLEDs are made up of the three primary colours (RGB), so there is a great gap (up to 100 nm) in the white-light spectrum, which means that the emission ranging from 520-620 nm is missing. White emission can be obtained based on the principle of additive colour mixing. Combination of blue and complementary yellow emissions is an attractive approach to reach white emission.³⁵ Concomitantly, guest molecule **5** represents a suitable binding partner for yellow iridium complex **2**, creating self-assembled hydrogen bonded systems, with preorganized arrangement that contributes to the stability of the **2•5** system. As defined by the CIE chromaticity system, an ideal white light has coordinates of $x=0.33$, $y=0.3334$ and can be realized by additive colour mixing.³⁶ Through synthesis of heteroleptic iridium complexes **3** and **4**, based on thiophenophenylquinoline derivatives as C^N ligands, red emission was targeted.

Recently, our team reported a series of iridium complexes with ancillary ligands based on guanidine and thiourea moieties, i.e., inherently H-bond rich motifs (Figure 2).²⁵ Through second-sphere coordination via H-bonding, we introduced a de novo strategy to alter photophysical properties of emitters, accessing a linear colour scale with a discretely interacting two component system, reaching into colour regions obviating the need of synthetic modifications around the metal centre.

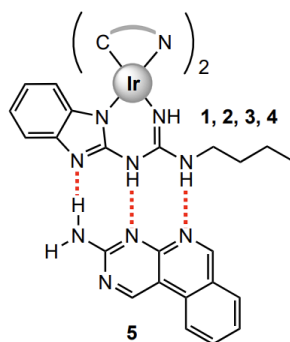


Figure 2. Proposed triple H-bonded systems, with preorganized arrangement that contributes to the stability of **1•5** to **4•5** systems.

Herein, we present the design and synthesis of yellow, orange/red and blue iridium complexes **1-4** (Figure 1) which provides potential strategies for colour tuning of PhOLEDs. This study led to the preparation of four new iridium complexes with various emission colours (Figure 3). All complexes were examined as single species and as co-systems in combination with previously reported guest molecule **5**.²⁵ Compound **5** represents a suitable binding partner for the guanidine and thiourea moieties that were combined with analogous iridium complexes²⁵ due to its ability to form triple H-bonded systems and modify the photophysical properties of such complexes.

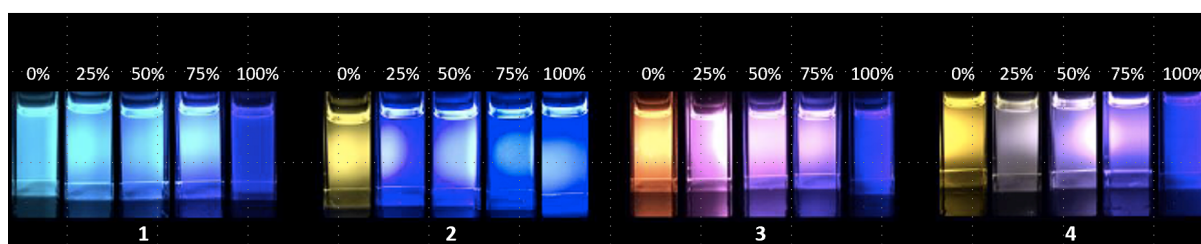


Figure 3. Vials from emission studies of iridium complexes **1-4** with added aliquots of compound **5**. Vials are illuminated with long wave UV-light (365 nm). Values in % corresponding to the molar equivalents of guest content (**5**) in solution.

Results and discussion

Synthetic details for the synthesis of compounds **1-5** are presented in the experimental section S1-2 (See supplementary information; SI). UV-Vis spectra of iridium complexes **1-4** were measured in CHCl₃ solution at the same concentration ($c=1.0 \times 10^{-5}$ M).

As shown in Figure S24 (SI), the absorption spectra of the four complexes are mainly comprised of three parts. Complexes **1-4** show relatively strong bands in the range of 250 to 350 nm, which can be attributed to spin-allowed singlet state ligand centred (¹LC) $\pi - \pi^*$ transitions. The central energy part in the absorption spectra from 350 to 450 nm can be ascribed to spin-allowed metal-to-ligand charge transfer singlet state ¹MLCT. The lowest energy component, extending 450 nm arises primarily from spin-forbidden ³MLCT transitions.³⁷ These types of electronic transitions are consistent with pertinent literature.³⁸⁻³⁹ The photoluminescence data, including emission maxima, lifetimes and quantum yields of complexes **1-4** are summarized in Table 1.

Table 1. a) Photoluminescence data for complexes **1-4**, all data was collected in CHCl₃ at degassed for 1 min (N₂) at 298 K. b) PLQYs for Ir(III) complexes **1-4**; in CHCl₃ degassed for 20 mins (Ar) at 298 K determined using the relative method. Further details of standard in appendix S1 and S5.

<i>Ir(III)</i> <i>complex</i>	Excitation Maxima (nm) ^a	Emission Maxima (nm) ^a	PLQY (%) ^b	Lifetime (ns) (τ_{PL}, χ^2) ^c	k_r ($\times 10^5 \text{ s}^{-1}$) ^d	k_{nr} ($\times 10^5 \text{ s}^{-1}$) ^d
1	378	467, 493	86.7	(2260.07, 1.057) (79%)	3.84	0.59
2	320	548, 583	8.7	(1.94, 1.029)	448.45	4706.19
3	293	570	23.4	(1703.39, 0.991) (65%)	1.38	4.50
4	289	594, 640	36.1	(3623.93, 0.976)	1.00	1.76

All complexes were studied as single species in CHCl₃ solutions and in combination with guest molecule **5**. Stacked emission spectra from the host-guest studies of complexes **1-4** in

combination with **5** are presented in the Appendix (Section x) and their association constants (K_a ; M^{-1}) summarized in Table 2. These high association constants can be explained through the use of Hammett values. Hammett values are used to parameterise the electron-withdrawing or donating ability of a substituent based on whether it is in a meta or para position to a particular functional group on the ligand, and so the position of the substituents, and the type of substituents (EDG & EWG) could have an effect on the strength of the association between the two molecules.⁴⁰ Since the H-bonding interactions are occurring between the guest molecule **5** and the ancillary ligand of the iridium complex, the cyclo-metallating ligands have minor effects on the K_a . More importantly, we must compare the association strength between systems with the same cyclo-metallating ligands, but different ancillary ligands.

Table 2. Association constants (M^{-1}) for Iridium complexes **1-4** H-bonding to guest molecule **5**. K_a and error determined by non-linear regression (via BindFit)⁴¹ of UV-Vis absorption data ($CHCl_3$:DMSO/99:1) at 298 K.

Co-System	$K_a \pm \sigma$
1•5	$6.8 \times 10^3 \pm 0.13 \%$
2•5	$6.1 \times 10^2 \pm 0.30 \%$
3•5	$6.5 \times 10^3 \pm 0.30 \%$
4•5	$1.1 \times 10^4 \pm 0.24 \%$

The H-bonding of compound **5** is not only used to measure the relative K_a 's of our Ir(III) compounds. The stoichiometric addition of **5** can tune the colour of the overall visible light emissions of our host guest systems.

The blue emission of complex **1** can be ascribed to the introduction of fluorine atoms on the C^N ligand, which generally stabilizes the HOMO orbital and leads to an increased HOMO-LUMO gap.³⁰ Upon excitation, emission of cyan-blue iridium **1** (CIE coordinates: x=0.18, y=0.31 and x=0.16, y=0.32, respectively) were modified by adding aliquots of **5** dissolved in a solvent system of CHCl₃ with 1% DMSO accessing a linear colour change reaching into deep blue region for 1:1 systems of CIE coordinates: x=0.15 and y=0.11, without the need to synthetically modify the structure of complex **1**. Additionally, changes in Φ_{PL} and lifetime values for complexes **1•5** in 1:1 solution would also serve as a preliminary proof of a mutual communication between the two species (host and guest) that are designed to form stable self-assembled H-bonded systems. For **1•5**, a decrease in quantum yield was observed (**1•5** in CHCl₃ solution Φ_{PL} =82.2 %) when compared with compound **1** (Φ_{PL} =86.7 %). The lifetime decay of complex **1** was measured to be 2.3 μs for the major component and decreased upon introduction of complement **5**. From the study of the **1•5** system in CHCl₃ solution, the longer lifetime component with value 2.1 μs was ascribed to the photoexcitation of complex **1** as the major component with a 97 % contribution. In addition, a fluorescence energy resonance transfer (FRET) experiment was conducted for **1•5** system in CHCl₃ solution. FRET represents a process where, after excitation, a donor molecule transfers its excited state energy to a neighbouring acceptor molecule.⁴² As presented in Figure 4, the emission intensity of compound **5** decreased and the emission intensity of complex **2** slightly increased after these two components were combined in 1:1 solution mixture. This study illustrates that compound **5** represents a donor molecule that can transfer its energy to complex **1** in the excited state.

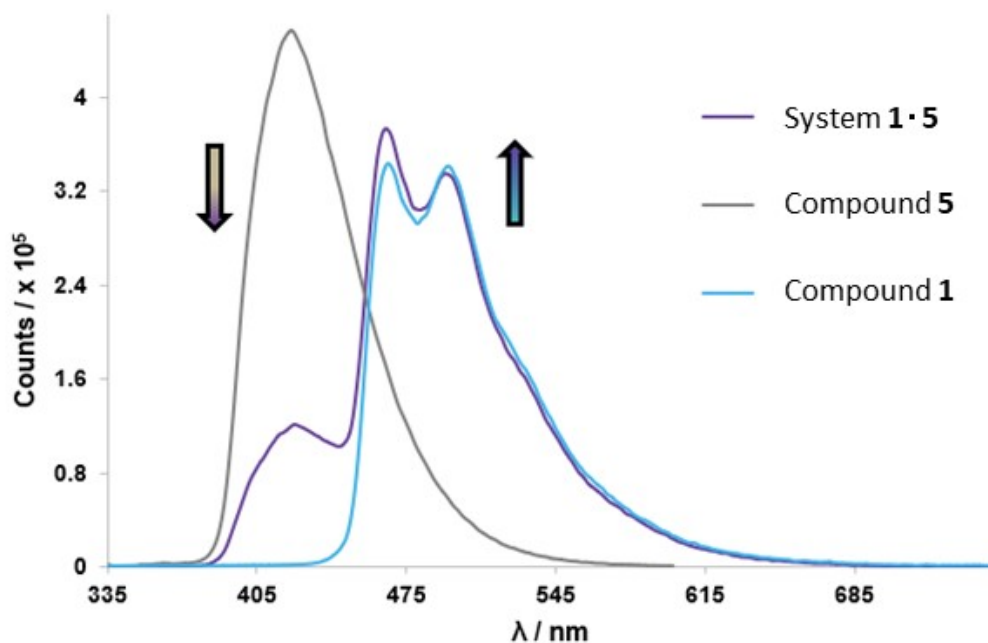


Figure 4. Overlaid emission spectra of complex **1** (blue), compound **5** (grey) and co-system **1•5** (purple) from FRET studies in CHCl_3 solution. All samples excited at $\lambda_{\text{ex}} = 325$ nm.

Ir(III) complex **2** emits yellow light while exhibiting low quantum yields and lifetimes. However, upon adding equivalents of compound **5** we see a gradual increase in quantum yield while maintaining its relatively low lifetimes leading to very high k_r and k_{nr} values in the **2•5** co-system. In particular, upon addition of 50 μL of a solution of **5** ($c=5 \times 10^{-5}$ M) to a solution of complex **4** (initial concentration $c=1 \times 10^{-4}$ M), white emission was achieved with CIE coordinates $x = 0.34$, $y = 0.33$ (**Figure. 5**). As mentioned previously, an ideal white light has coordinates of $x=0.33$ and $y=0.33$.³⁴ Considering the low quantum yield for complex **2** ($\Phi_{\text{PL}}=3.4\%$), it was expected to have a shorter excited state lifetime ($\tau = 1.94$ ns). The quantum yield increased to $\Phi_{\text{PL}}=15.6\%$ after addition of compound **9** when measured as 1:1 co-system **2•5** in CHCl_3 solution. When the system is re-measured with a ratio of 1:1.3 in the co-system **2•5**, the system gives near pure white light emission the quantum yield increased dramatically ($\Phi_{\text{PL}}=33.2\%$) while maintaining a relatively low lifetime of 3.37 ns leading to high radiative and non-radiative decay constants for white light emission. This ratio used in

white light testing was obtained by a combination of practical and theoretical techniques, for the final ratio a titration of compound **5** and Ir complex **2** was undertaken (**Figure 6.**). To determine appropriate starting concentrations for the titration to determine molar ratio, a previously reported technique was implemented to estimate the overall contributions of **2** and **5** to the co-system.

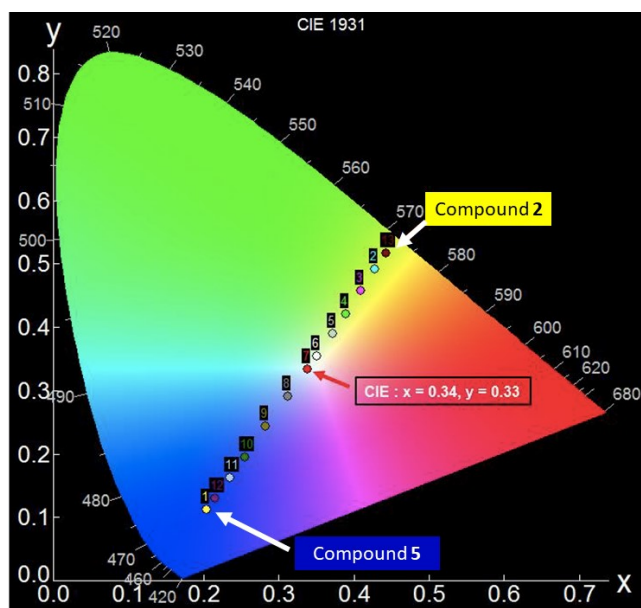


Figure 5. CIE diagram from fluorescence titration experiment of host complex **2** and guest compound **5**.

The following equation developed by Price *et al.*⁴² allows for the molar equivalents required in specific colour tuned emissions to be estimated to a high degree of accuracy. The equation takes into account the PL contributions of the multiple components into a linear combination *or relative brightness* (a_i) as the product of the i th components mole fraction (χ_i), photoluminescent quantum yield (Φ_i), and excitation intensity ($I_{ex,i}$) at a common wavelength.

$$(x_{(mix)}, y_{(mix)}) = a_1(x_1 + y_1) + a_2(x_2, y_2) + \dots + a_i(x_i + y_i)$$

$$a_i = \frac{\chi_i \Phi_i I_{ex,i}(\lambda_{ex})}{\sum_{i=1}^n \chi_i \Phi_i I_{ex,i}(\lambda_{ex})}$$

The equation can only be used for a rough estimation of correct ratio within the co-system for white light emission, this is because the equation does not take into account energy transfer within co-systems such as those presented herein between our H-bonding binder compound **5** and all Ir complexes **1-4**. Upon use of the equation, we determined the theoretical molar ratio for white light emission was 1:1.41, which is a significant difference from our practically obtained molar ratio of 1:1.3 showing energy transfer within the co-system **2•5**.

Table 3. a) Photoluminescence data for complexes **1-4** titrated with **5**, all data was collected in CHCl₃ at degassed for 1 min (N₂) at 298 K. b) PLQYs for Ir(III) complexes **1-4**; in CHCl₃ degassed for 20 mins (Ar) at 298 K determined using the relative method. Further details of standard in appendix S1 and S5.

<i>Ir(III)</i> <i>complex</i>	Excitation Maxima (nm)^a	Emission Maxima (nm)^a	PLQY (%)^b	Lifetime (ns) (τ_{PL}, χ^2)^c	k_r (x 10⁵ s⁻¹)^d	k_{nr} (x 10⁵ s⁻¹)^d
1•5 (1:1)	280	425, 462	82.2	(2088.43, 0.922) (97%)	0.39	0.85
2•5 (1:1)	310	538, 584	15.6	(3.62, 1.186)	430.94	2331.49
3•5 (1:1)	298	570	43.3	(4298.43, 0.972) (90%)	1.01	1.32
4•5 (1:1)	295	596, 638	41.4	(3586.05, 0.994) (99%)	1.15	1.63
2•5 (1:1.3)	308	538, 584	33.2	(3.37, 1.372)	985.16	1982.20

Iridium complexes **3** and **4** were synthesized in order to study orange/red emissive complexes and their communication with compound **5** via energy transfer. Specifically, the energy transfer efficiency for systems **3•5** and **4•5** was measured and calculated to be approximately 36 % and 35 %, respectively. The energy transfer (ET) values were calculated from the ratio between the corrected excitation spectrum of host-guest pairs and their absorption spectra. Emission spectra of systems **3•5** and **4•5** in CHCl₃ solution were collected at a higher wavelength $\lambda_{ex} = 640$ nm, which is beyond the emission window of guest compound **5**. From

the calculations, we observed that the ET efficiency for **3•5** was approximately 36 % from the ratio between the corrected excitation spectrum of **3•5** (Figure. 7).

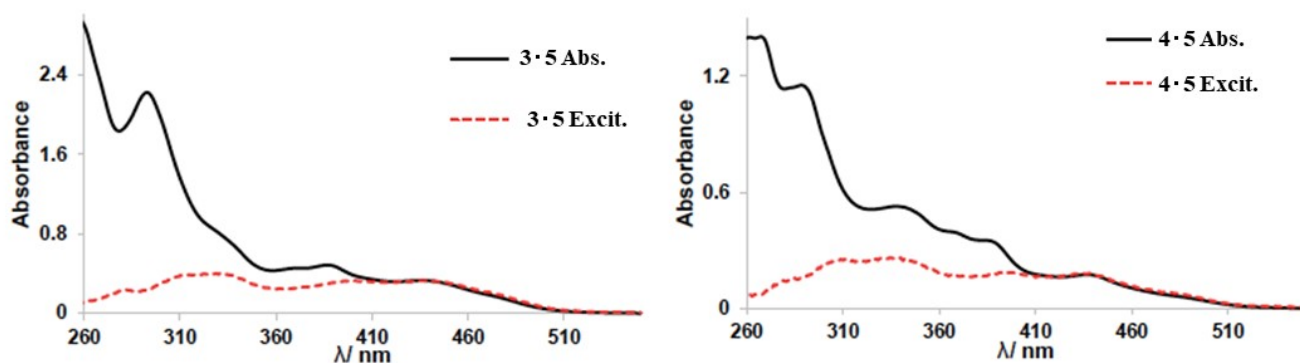


Figure 6. Absorption (solid black line) and corrected PL excitation (red dashed line measured at 570 nm) for co-system **3•5** (left) and **4•5** (right) (1:1 ratio of Ir complex and compound **5**). Spectra normalized to absorbance at 440 nm.

The ET calculated for co-system **4•5** was calculated to be 35 % which represents an almost identical value as for system **3•5** (36 %). From this study, it can be concluded that even if the emission properties of complexes **3** and **4** were slightly different (shift in emission maxima ~ 20 nm), their energy transfer efficiency values when combined with compound **5** are identical. Furthermore, these experiments demonstrated that there is a sufficient distance for “communication” between complexes **3/4** and guest compound **5** in 1:1 solution. To further examine communication of complexes **3/4** with **5**, emission spectra of 1:1 mixture in CHCl_3 solutions were collected. For both systems **3•5** and **4•5**, we observed a FRET effect. As mentioned before, FRET occurs when energy absorbed by a donor molecule is transferred to a nearby acceptor molecule.

As shown in Table 3 there was a slight increase in the photoluminescence quantum yields measured for the solutions of **3•5** and **4•5** when compared to the values of the single complex systems in Table 1. The quantum yields increased for both complexes **3** and **4** when introduced to **5** in a co-system, **3** had a more significant change when in the co-system with

the quantum yield increasing from 23.4 % to 43.3 %. As presented in Table 3, the lifetime decays for both systems **3•5** and **4•5** were increased when guest compound **5** was introduced to the systems. The longer lifetimes (4298.43 ns and 3586.05 ns), which are ascribed to the direct photoexcitation of the complexes **3** and **4**, represent the major components with contributions of 90 % and 99 %, respectively.

Conclusions

In conclusion, we have demonstrated the design, synthesis and characterization of four novel heteroleptic Ir (III) complexes bearing a benzimidazole-linked guanidine ligands allowing for a high degree of colour tuneability. Each iridium complex (**1-4**) was further studied to demonstrate a unique property when combined with compound **5**. Emission of cyan-blue complex **1** can be modified (accessing a deep blue emission)²⁷ through addition of compound **5**. Yellow complex **2** demonstrated white light emission (CIE coordinates: x=0.33, y=0.34) after controlled addition of compound **5** in solution. Moreover, an increased quantum yield (from $\Phi_{\text{PL}} = 8.7\%$ for complex **2** to 33.2% for co-system **2•5** (1:1.3)) in solution was observed during the photoluminescence studies. Complexes **3** and **4** were studied as cyclometallated ligands for red emitting Ir (III) complexes bearing guanidine moieties within the structures. Iridium complexes with red emission are desirable in PhOLED applications as well as bio-imaging.³¹⁻³² Particularly, complex **4** bearing a less conjugated cyclometallated ligand than complex **3**, showed desirable red emission with $\lambda_{\text{em}} = 593$ nm and a shoulder peak at 640 nm in CHCl₃ solution. ET efficiency was calculated for both complexes **3** and **4** when mixed with compound **5** in 1:1 CHCl₃ solution (35% for system **3•5** and 36% for system **4•5**). The FRET effect in systems **3•5** and **4•5** was studied and confirmed the ability of compound **5** to act as donor of energy, when mixed in 1:1 ratio with complex **3** or **4** in solution. Future plans for complexes **3** and **4** include the examination of their properties for biological applications as they contain thiourea and guanidine moieties, which

represents an available binding site for appropriate guest molecules in supramolecular hydrogen bonded systems.

Author Contributions

BB: conceptualization, methodology, investigation, formal analysis, data curation, writing – original draft. THJ: investigation, validation, writing. AET investigation, formal analysis, validation. SMH: investigation, validation. BAB: funding procurement, conceptualization, writing.

Funding Sources

We gratefully acknowledge the University of New Brunswick, and its Department of Chemistry for financial and technical support. This work was fully supported by Natural Science and Engineering Council of Canada (NSERC; DG RGPIN-2018-04021) and New Brunswick Foundation for Innovation (NBIF; RAI-2019-023).

Competing Interests

The authors declare no conflicts of interest.

References

- 1 Z. Lu, M. Shangguan, X. Jiang, P. Xu, L. Hou and T. Wang. *Dye Pigment.*, 2019, **171**, 107715.
- 2 K. Y. Zhang, P. Gao, G. Sun, T. Zhang, X. Li, S. Liu, Q. Zhao, K. K.-W. Lo and W. Huang. *J. Am. Chem. Soc.*, 2018, **140**, 7827-7834.
- 3 K. Fan, S.-S. Bao, W.-X. Nie, C.-H. Liao and L.-M. Zheng. *Inorg. Chem.*, 2018, **57**, 1079-1089.
- 4 Q. Wu, Y. Cheng, Z. Xue, X. Gao, M. Wang, W. Yuan, S. Huettner, S. Wan, X. Cao, Y. Tao and W. Huang. *Chem. Commun.*, 2019, **55**, 2640-2643.
- 5 E. Baranoff, P. Kumar, in *Iridium (III) in Optoelectronic and Photonics Applications*, John Wiley & Sons, Ltd, Chichester, UK, 2017, pp. 655-681.
- 6 X.-S. Gu, N. Yu, X.-H. Yang, A.-T. Zhu, J.-H. Xie and Q.-L. Zhou. *Org. Lett.*, 2019, **21**, 4111-4115.

- 7 S.-M. Lu, Z. Wang, J. Wang, J. Li, and C. Li. *Green Chem.*, 2018, **20**, 1835-1840.
- 8 a) I. Omae. *Coord. Chem. Rev.*, 2016, **310**, 154-169. b) T.-Y. Li, J. Wu, Z.-G. Wu, Y.-X. Zheng, J.-L. Zuo and Y. Pan. *Coord. Chem. Rev.*, 2018, **374**, 55-92.
- 9 S. Guo, T. Huang, S. Liu, K. Y. Zhang, H. Yang, J. Han, Q. Zhao and W. Huang. *Chem. Sci.*, 2017, **8**, 348-360.
- 10 X. Liu, B. Yao, Z. Zhang, X. Zhao, B. Zhang, W.-Y. Wong, Y. Cheng and Z. Xie. *J. Mater. Chem. C.*, 2016, **4**, 5787-5794.
- 11 H. Benjamin, M. A. Fox, A. S. Batsanov, H. A. Al-Attar, C. Li, Z. Ren, A. P. Monkman and M. R. Bryce. *Dalt. Trans.*, 2017, **46**, 10996-11007.
- 12 S. Y. Lee, T. Yasuda, Y. S. Yang, Q. Zhang, C. Adachi. *Angew. Chem. Int. Ed.*, 2014, **53**, 6402-6406.
- 13 Y. You and S. Y. Park. *Dalt. Trans.*, 2009, 1267-1282.
- 14 N.-Y. Chau, P.-Y. Ho, C.-L. Ho, D. Ma, W.-Y. Wong. *J. Organomet. Chem.*, 2017, **829**, 92-100.
- 15 A. F. Henwood and E. Zysman-Colman. *Chem. Commun.*, 2017, **53**, 807-826.
- 16 C. Hierlinger, D. B. Cordes, A. M. Z. Slawin, D. Jacquemin, V. Guerschais, E. Zysman-Colman. *Dalt. Trans.*, 2018, **47**, 10569-10577.
- 17 J. R. Shakirova, O. A. Tomashenko, E. E. Galenko, A. F. Khlebnikov, P. Hirva, G. L. Starova, S.-H. Su, P.-T. Chou, S. P. Tunik. *Inorg. Chem.*, 2018, **57**, 6853-6864.
- 18 I. R. Laskar, T.-M. Chen. *Chem. Mater.*, 2004, **16**, 111-117.
- 19 S. Takizawa, J. Nishida, T. Tsuzuki, S. Tokito, Y. Yamashita. *Inorg. Chem.*, 2007, **46**, 4308-4319.
- 20 Y. Wang, N. Sun, B. F. E. Curchod, L. Male, D. Ma, J. Fan, Y. Liu, W. Zhu, E. Baranoff. *J. Mater. Chem. C.*, 2016, **4**, 3738-3746.
- 21 C.-J. Li, S.-Y. Yin, H.-P. Wang, Z.-W. Wei, M. Pan. *J. Photochem. Photobiol. A Chem.*, 2019, **379**, 99-104.
- 22 a) F.-M. Hwang, H.-Y. Chen, P.-S. Chen, C.-S. Liu, Y. Chi, C.-F. Shu, F.-I. Wu, P.-T. Chou, S.-M. Peng, G.-H. Lee. *Inorg. Chem.*, 2005, **44**, 1344-1353. b) G. Li, D. G. Congrave, D. Zhu, Z. Su, M. R. Bryce. *Polyhedron*, 2018, **140**, 146-157.

- 23 W.-K. Hu, S.-H. Li, X.-F. Ma, S.-X. Zhou, Q. Zhang, J.-Y. Xu, P. Shi, B.-H. Tong, M.-K. Fung and L. Fu. *Dye. Pigment.*, 2018, **150**, 284-292. b) J. Yao, S. Ying, Q. Sun, Y. Dai, X. Qiao, D. Yang, J. Chen and D. Ma. *J. Mater. Chem. C*, 2019, **7**, 11293-11302.
- 24 P.-N. Lai, C. H. Brysacz, M. K. Alam, N. A. Ayoub, T. G. Gray, J. Bao, T. S. Teets. *J. Am. Chem. Soc.*, 2018, **140**, 10198-10207.
- 25 B. Balónová, D. Rota Martir, E. R. Clark. H. J. Shepherd, E. Zysman-Colman and B. A. Blight. *Inorg. Chem.*, 2018, **57(14)**, 8581-8587.
- 26 A. K. Pal, S. Krotkus, M. Fontani, C. F. R. Mackenzie, D. B. Cordes, A. M. Z. Slawin, I. D. W. Samuel, E. Zysman-Colman. *Adv. Mater.*, 2018, **30**, 1804231.
- 27 T. Smith, J. Guild. *Trans. Opt. Soc.*, 1931, **33**, 73-134.
- 28 X. Yang, X. Xu, G. Zhou. *J. Mat. Chem. C.*, 2015, **3**, 913-944.
- 29 J.-H. Lee, G. Sarada, C.-K. Moon, W. Cho, K.-H. Kim, Y. G. Park, J. Y. Lee, S.-H. Jin and J.-J. Kim. *Adv. Opt. Mater.*, 2015, **3**, 211-220.
- 30 Y. Miao, P. Tao, L. Gao, X. Li, L. Wei, S. Liu, H. Wang, B. Xu and Q. Zhao. *J. Mater. Chem. C.*, 2018, **6**, 6656-6665.
- 31 J. Zhu, B. Z. Tang and K. K. Lo. *Chem.: A Eur. J.*, 2019, **25**, 10633-10641.
- 32 V. Venkatesh, R. Berrocal-Martin, C. J. Wedge, I. Romero-Canelon, C. Sanchez-Cano, J.-I. Song, J. P. C. Coverdale, P. Zhang, G. J. Clarkson, A. Habtemariam, S. W. Magennis, R. J. Deeth, P. J. Sadler. *Chem. Sci.*, 2017, **8**, 8271-8278.
- 33 S. Wang, Q. Yang, B. Zhang, L. Zhao, D. Xia, J. Ding, Z. Xie, L. Wang. *Adv. Opt. Mater.*, 2017, **5**, 1700514.
- 34 H. Wu, L. Ying, W. Yang, Y. Cao. *Chem. Soc. Rev.*, 2009, **38**, 3391-3400.
- 35 P. Tao, W.-L. Li, J. Zhang, S. Guo, Q. Zhao, H. Wang, B. Wei, S.-J. Liu, X.-H. Zhou, Q. Yu, B.-S. Xu and W. Huang. *Adv. Funct. Mater.*, 2016, **26**, 881-894.
- 36 K. T. Kamtekar, A. P. Monkman, M. R. Bryce. *Adv. Mater.*, 2010, **22**, 572-582.
- 37 a) P.-N. Lai, C. H. Brysacz, M. K. Alam, N. A. Ayoub, T. G. Gray, J. Bao, T. S. Teets. *J. Am. Chem. Soc.*, 2018, **140**, 10198-10207. b) Y.-J. Cho, S.-Y. Kim, C. M. Choi, N. J. Kim, C. H. Kim, D. W. Cho, H.-J. Son, C. Pac, S. O. Kang. *Inorg. Chem.*, 2017, **56**, 5305-5315.

- 38** H. Zhen, C. Luo, W. Yang, W. Song, B. Du, J. Jiang, Y. Zhang and Y. Cao. *Macromolecules*, 2016, **39**, 1693-1700.
- 39** L. Zhao, S. Wang, L. Lu, J. Ding and L. Wang. *J. Mater. Chem. C.*, 2017, **5**, 9753-9760.
- 40** Hollingsworth, C. A.; Seybold, P. G.; Hadad, C. M. Substituent Effects on the Electronic Structure and PKa of Benzoic Acid. *International Journal of Quantum Chemistry* 2002, **90** (4-5), 1396–1403.
- 41** P. Thordarson. *Chem. Soc. Rev.*, 2011, **40(3)**, 1305-1323.
- 42** Price, J.; Barbora Balónová; Blight, B. A.; Eisler, S. *Chemical Science* 2021, **12** (36), 12092–12097.