

Exploring Energy Transfer in Luminescent Heterometallic Ruthenium-Iridium Ion Pairs

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Abstract. Here, we report the synthesis of a luminescent ion pair with the formula $[\text{Ru}(\text{dtbubpy})_3][\text{Ir}(\text{ppy})_2(\text{CN})_2]_2$. The crystal structure of this three component, heterometallic assembly is described, along with the luminescence properties of the salt. The modulation of the energy transfer between the blue-emitting iridium complex and the red-emitting ruthenium complex is also discussed as a function of both medium and concentration.

Introduction. Energy and electron transfer dynamics between donor-acceptor dyads are extremely important in energy conversion applications. Solar cells¹ and solar fuels² frequently rely on such architectures. Conversely, white-light emitting devices such as organic light-emitting diodes (OLEDs)³ and light-emitting electrochemical cells (LEECs)⁴ are fabricated from host-guest mixtures of complementary emissive mixtures of compounds (usually red and blue emitters) where the design strategy is predicated on limiting energy transfer between subunits. Thus, pre-organization of host-guest systems is key to the control of energy transfer.

Ordered, supramolecular assemblies incorporating iridium(III) are rare, the examples of which are mostly limited to capsules,⁵ coordination assemblies and networks⁶ and MOFs.⁷ Recently, five accounts of closely related homometallic luminescent ion pairs involving iridium have been reported.⁸ These complex salts, composed of two photo- and electroactive coordination complexes, having opposite charges, were called “soft salts” by Thompson et al. due to the soft nature of the ions.^{8a} In the complex salt or “soft salt” reported by De Cola,^{8b} the system formed a porous network in the crystalline solid state. Emission in the crystal was red-shifted compared to the mononuclear ion with the lowest-energy excited state due to exciplex formation promoted by strong π -stacking interactions between the ions. Concentration-dependent energy transfer between the ions in acetonitrile solution was shown by Thompson and co-workers to proceed via a Dexter mechanism. The same group fabricated OLEDs and found that external quantum efficiencies varied considerably but could be optimized when the HOMO and LUMO levels of one ion were sandwiched in between those of the other;^{8a} LEEC devices were non operational due to the large size and poor mobility of the ions.

Herein, we report the first example of a three component heterometallic ion pair assembly $[2][1]_2$ involving two equivalents of a blue-emitting $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ (**[1]**) associated with red-emitting $[\text{Ru}(\text{dtbubpy})_3]^{2+}$ (**[2]**) (ppyH = 2-phenylpyridine; dtbubpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) and compare its photophysical behavior with the mononuclear complexes **TBA[1]** and **[2]Cl₂**, (Chart 1). The motivation for the present study is to investigate the modulation of the energy transfer processes between these two complementary emitters, in the context of research in white-emitting molecular systems.

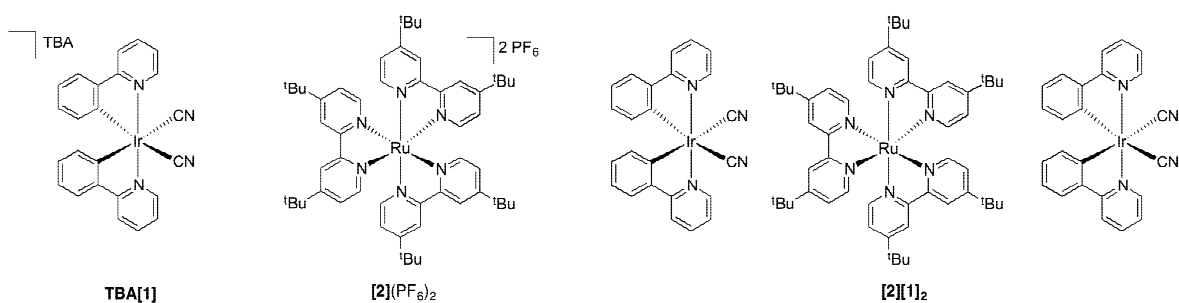


Chart 1. Chemical structures of **TBA[1]**, **[2](PF₆)₂** and **[2][1]₂**.

Results and Discussion. Though complex salts or mixtures of salts incorporating a ruthenium complex (usually acting as the donor) have been studied for some time,⁹ we chose to investigate $[2][1]_2$ due to the complementary optoelectronic properties of its constituent ions (emission color and HOMO/LUMO energies as determined by cyclic voltammetry (CV)). The ion pair was formed through reaction of a 2:1 stoichiometric mixture of **TBA[1]** and **[2]Cl₂** in dichloromethane (DCM). The counter ions were removed through repeated water washes. The correct stoichiometry was confirmed by ¹H-NMR and UV-Vis titration experiments (Figure S3). The presence of both ions was corroborated by ESI-HRMS running in both positive and negative ion modes.

Complex salt **[2][1]₂** was crystallized by vapor diffusion from acetonitrile (ACN) and *tert*-butyl methyl ether (TBME) (Figure 1). The translucent orange prisms are monoclinic and crystallized in the C1 2/n 1 space group as an ACN and TBME solvate. The relevant structural parameters for both **[1]**¹⁰ and **[2]**^{6c, 8b} are similar to those found in related mononuclear crystal structures. The TBME molecules and certain ACN molecules are disordered but are located in channels along the crystallographic *b*-axis. The resulting Ru^{III}-Ru distance across the channel is 17.2653(8) Å. The volume within the unit cell is 12219.3(10) Å³, which is six times larger than that found the complex salt reported by De Cola. Of that volume, 33.6% or 4109.5 Å³ is void space. The two molecules of **[1]** are symmetry related about a C₂ axis and are oriented to maximize the electrostatic interaction with **[2]**. There are short contacts between the cyano nitrogen atoms of **[1]** and hydrogen atoms of the dtbubpy ligands of **[2]**. One of the CN ligands of **[1]** is oriented parallel to the crystallographic *a*-axis and is positioned as to promote a three-center interaction with the 3 and 3' protons of one of the dtbubpy ligands [N_{CN}(**[1]**)-H³_{dtbubpy} = 2.664(6), N_{CN}-H^{3'}_{dtbubpy} = 2.594(8) Å] while the second CN ligand is anchored through both a dipolar- π interaction (distance from centroid of dtbubpy to N_{CN}(**[1]**) = 3.340 Å) and a hydrogen bond between H⁶_{dtbubpy} of a second dtbubpy ligand and N_{CN}(**[1]**) (2.449(6) Å). Successive molecules of **[2][1]₂** are held together through a slipped π -stacking interaction along the crystallographic *a*-axis of antiparallel ppy ligands of adjacent molecules of **[1]** with centroid-to-centroid distances of 3.894 Å between adjacent phenyl rings. The intermetallic Ru^{III}-Ir distance in **[2][1]₂** is 7.0111(4) Å, significantly shorter than that observed in the complex salt of De Cola (Ir^{III}-Ir = 8.690(2) Å), suggesting much tighter binding due to enhanced electrostatic interactions in our case.

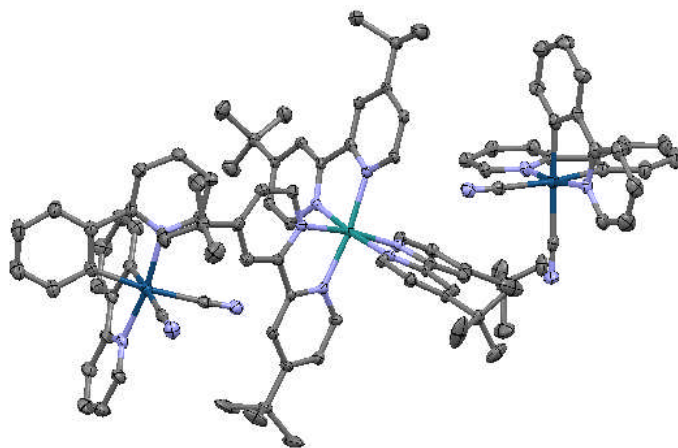


Figure 1. ORTEP representation (30% probability) of the structure of $[2][1]_2$. Solvent molecules and hydrogen atoms have been removed for clarity.

The UV-Visible absorption spectrum of the soft salt, recorded in ACN, shows the characteristic features of both ions (Figure 2). The visible absorption centered at 458 nm is due to the broad $^1\text{MLCT}$ transition ($d_{\text{Ru}} \rightarrow \pi^*_{\text{dtbubpy}}$) while in the UV region the spectrum is dominated by intense ligand-centered bands (^1LC) for both complexes. No significant shifts were observed in ACN with respect to the single components (**TBA[1]** and **[2]Cl₂**). As expected, the absorption profile of $[2][1]_2$ superimposes well with that of the control mixture solution (**TBA[1]** : **[2]Cl₂** = 2:1) and with the mathematical sum of the absorption spectra of 2 equiv. of **TBA[1]** and 1 equiv. of **[2]Cl₂** (Figure S3), which establishes unequivocally the composition of the soft salt.

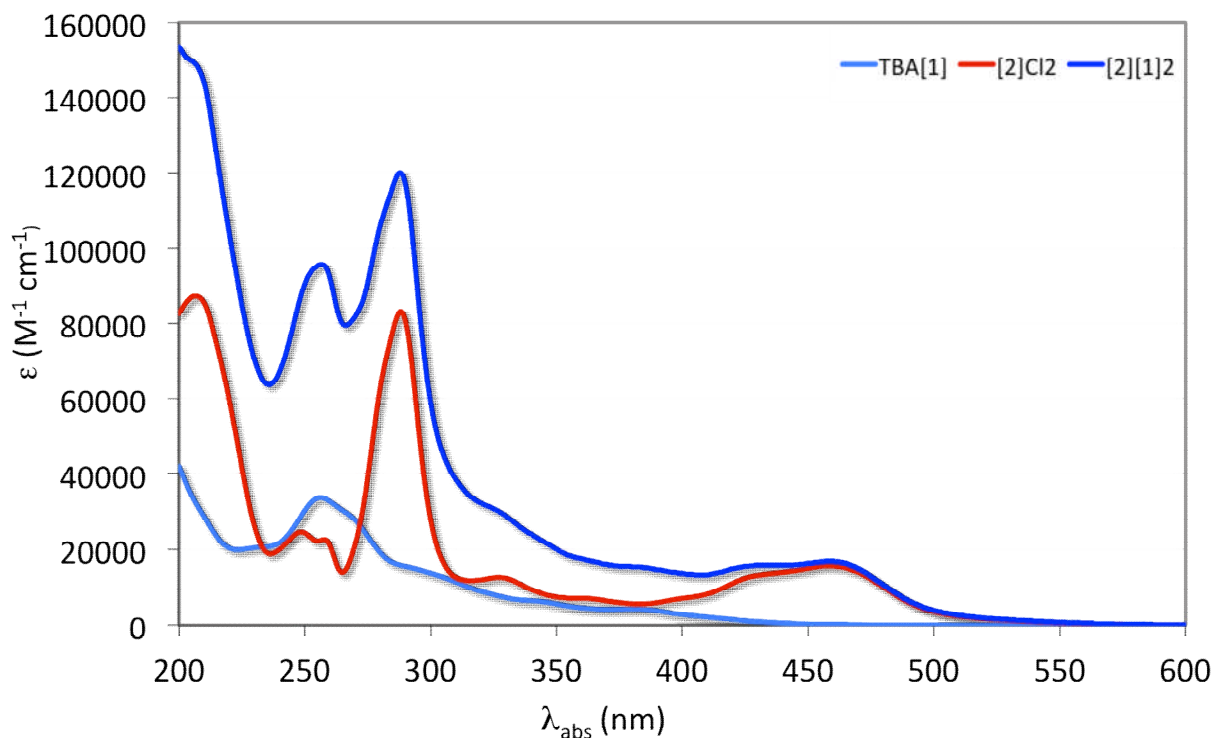


Figure 2. UV-Visible absorption spectra of the soft salt **[2][1]₂** and the mononuclear components **TBA[1]** and **[2]Cl₂**, recorded in aerated acetonitrile at 298 K.

Upon excitation into the ¹MLCT band, **[2]Cl₂** exhibits the characteristic broad red emission from the ³MLCT state centered at 630 nm, covering a spectral window from 550 to 800 nm. **TBA[1]**, on the other hand, displays a structured ³LC blue phosphorescence ($E_{0,0}(\text{ACN}) = 477$ nm, 2.60 eV), tailing off at 600 nm. The spectra of the mononuclear complexes are shown in Figure **S4** (a) and (b).

The emission properties of the soft salt are of particular interest as the two ions have complementary emission. The modulation of the relative intensity of the emission bands, in fact, is particularly germane in the context of white-emitting materials. Double electron exchange through a Dexter energy transfer (ET) between the two phosphors mediated by collision is

certainly possible. However, the good overlap between the $^1\text{MLCT}$ and $^3\text{MLCT}$ absorption bands of the Ru complex, **[2]**, (energy acceptor) and the emission of the Ir complex, **[1]**, (energy donor) meets the requirements to have Förster resonant ET, a situation not possible in the other Ir-based soft salts reported to date. Förster ET though rare is not unprecedented in Ir emitters.¹¹ Solvent polarity is expected to strongly influence the strength of the electrostatic interaction between the two ions and thus the intermolecular distance in solution.¹² We therefore decided to investigate the impact of this factor on the radiative decay of **[2][1]₂** to check if it could be used to control and modulate the emission profile of the salt, in order to extend it over the whole visible spectrum.

Due to the absorption profiles of **TBA[1]** and **[2]Cl₂**, only selective excitation of **[2]** is possible. The emission spectra for the soft salt were thus obtained by exciting the solution at either the maximum of the $^1\text{MLCT}$ band of **[2]** (λ_{exc} : 458-461 nm, see Table S1) or at 390 nm, where **[1]** and **[2]** are isoabsorptive in ACN (similar ϵ values). In general, only the broad $^3\text{MLCT}$ red emission from **[2]** is observed upon excitation at ca. 460 nm, while both the structured blue emission from **[1]** and red emission from **[2]** are apparent when the soft salt is excited at 390 nm.

The relative intensity (and by extension the degree of electronic coupling) of the emission bands associated with **[1]** and **[2]** is strongly influenced by solvent polarity (Figure 3) and concentration (Figure 4). The relative intensity of the Ir-based emission in **[2][1]₂** decreases markedly in low polarity solvents to the point of being less intense than the Ru-based red phosphorescence. The same phenomenon is observed in ACN solution at high concentrations. In both cases, conditions are thought to promote the formation of an intimate ion pair, resulting in a

shorter distance between the Ir and Ru ions. The energy transfer thus becomes more efficient. Notably, in 2-methyltetrahydrofuran (2-MeTHF) solution and in the solid state, a red shift in the Ru emission was observed, implying the formation of excimers or exciplexes in these media.¹³ The modulation of the relative intensity of two emission bands covering, respectively, the blue-green, [1], and the red part, [2], of the visible spectrum is important as it permits a fine control of the color of the light emitted by the soft salts. This result, usually achieved by tuning the ratio between the two luminescent ions, is here obtained by simply choosing the appropriate solvent or concentration. For instance, the overall color of the emitted light spans from light blue to orange-red, passing through near-white emission as illustrated in Figure 4 and Figure S10.

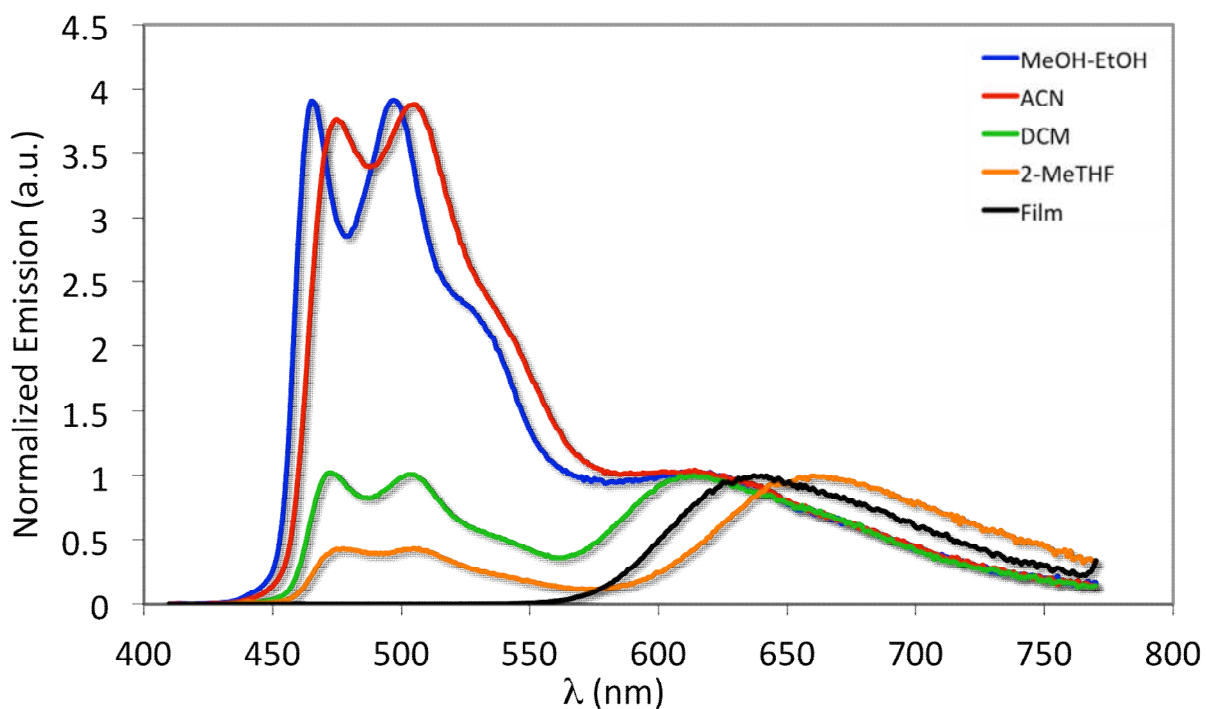


Figure 3. Emission spectra of [2][1]₂ recorded in different solvents ($\sim 2 \times 10^{-5}$ M) and in the solid state, normalized on the Ru emission band (λ_{em} : 617-663 nm). λ_{exc} : 390 nm.

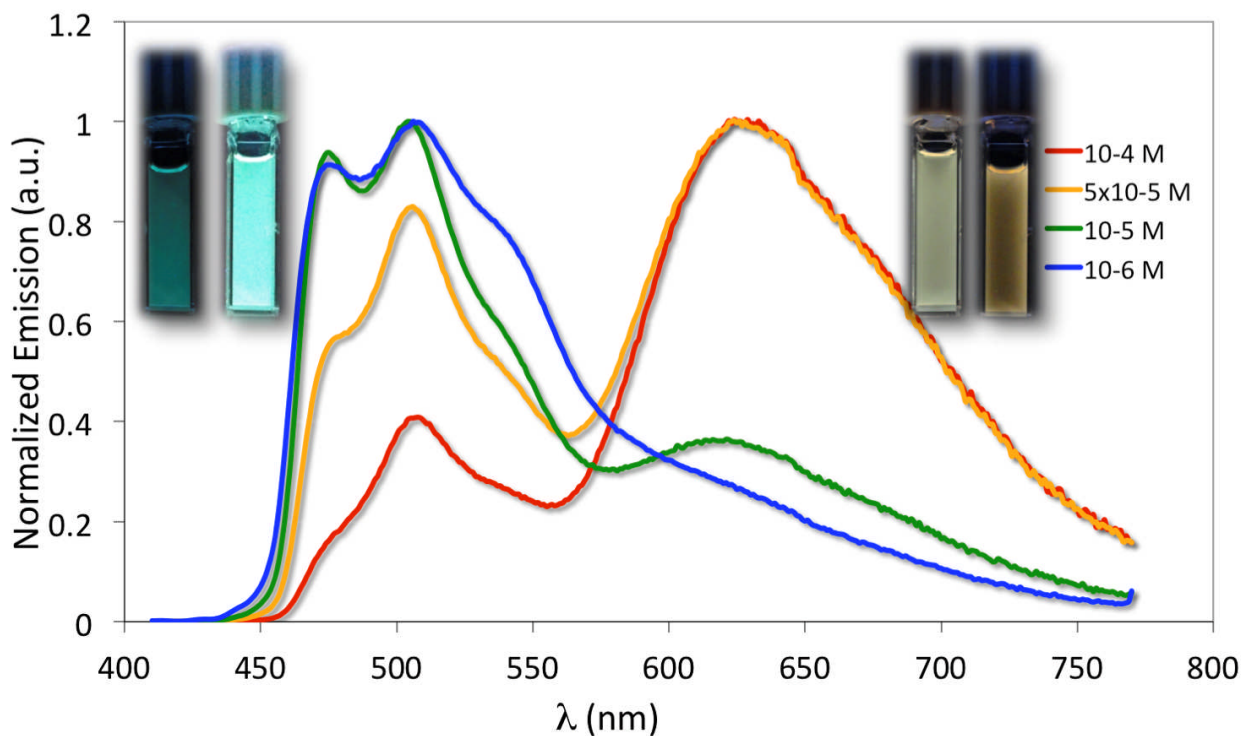


Figure 4. Normalized emission spectra of $[2][1]_2$ recorded in deaerated ACN at 298 K at different concentrations. $\lambda_{\text{exc}} = 390 \text{ nm}$; $A_{390} = 0.09$. Insets are images of ACN solutions of $[2][1]_2$ at different concentrations. The remarkable profile change at elevated concentrations is ascribed to an inner filter effect due to the absorption of $[2]$ at 458 nm.

A Stern-Volmer analysis was carried out in both ACN and DCM in order to elucidate the bimolecular quenching constant (Figure S5). Quenching constants of 3.9×10^{10} and $3.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ were obtained in ACN and DCM, respectively, as the ratio between K_{SV} and τ_0 , the lifetime of **TBA[1]** in the absence of quencher. These values are close to the value of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, indicating that the process is diffusion-controlled.¹⁴ However, it should be noted that in this analysis counterions were present, which reduces the possibility of aggregation between the two photoactive ions. This explains the similar values obtained in the two solvents, while the

emission behavior of the soft salt under the same conditions was quite distinct (Figure 3). To further clarify the role played by the counterions, a partial recovery of the iridium emission was observed in a DCM solution of **[2][1]₂** after addition of 2 equivalents of TBACl, while nearly no change was noticed when the same experiment was carried out in ACN. In the first case, the two complexes are believed to be more tightly associated due to the poorer coordinating capacity of the solvent, and the small counterions are able to disrupt the electrostatic interactions between **[2]²⁺** and **[1]⁻**, impeding the energy transfer process (Figure S6).

Time-resolved luminescence measurements were carried out on the two model complexes and on the salt (Table 1) in order to elucidate the effect of energy transfer on the emission lifetime, τ_e , of the two emissive ions. The values obtained for **TBA[1]** and **[2]Cl₂** are in good agreement with those reported in literature.^{10, 15} Surprisingly, **TBA[1]** exhibited a much longer τ_e in alcoholic solution. This change in behavior was rationalized due to hydrogen bonding interactions between both ions with the solvent molecules.

Table 1. Emission lifetime data.^[a]

Complex	Solvent	τ_e (μ s)	Φ_{PL} (%)
TBA[1]	MeOH/EtOH ^[b]	5.47 ^[c]	64 ^[g]
	CH ₃ CN	3.13 ^[c]	
	CH ₂ Cl ₂	3.26 ^[c]	
	2-MeTHF	2.43 ^[c]	
[2]Cl₂	MeOH/EtOH ^[b]	0.853 ^[d]	11 ^[h]
	CH ₃ CN	0.871 ^[d]	

	CH ₂ Cl ₂	0.956 ^[d]	
	2-MeTHF	0.797 ^[e]	
[2][1] ₂	MeOH/EtOH ^[b]	2.66 (46%); 0.815 (54%) ^[c]	
		2.74 (32%); 0.824 (68%) ^[f]	
	CH ₃ CN	2.09 (59%); 0.898 (41%) ^[c]	30 ^[g]
		2.11 (37%); 0.913 (63%) ^[f]	
	CH ₂ Cl ₂	1.39 (83%); 0.691 (17%) ^[c]	
		1.52 (38%); 1.07 (62%) ^[f]	
	2-MeTHF	0.485 (35%); 0.849 (65%) ^[c]	
		0.655 (100%) ^[f]	

[a] Emission lifetimes recorded at 298 K under an Ar atmosphere ($\lambda_{exc} = 405$ nm); [b] Solvents in a 1:1 ratio; [c] detection with filter at 475-525 nm; [d] detection with filter at 525-575 nm; [e] emission at 630 nm of [2](PF₆)₂, the chloride salt is insoluble in 2-MeTHF; [f] detection with filter at 575-625 nm; [g] Φ_{PL} standard: quinine sulfate in 1N H₂SO₄, $\Phi_{PL} = 54.6\%$; ¹⁶ [h] Φ_{PL} standard: [Ru(bpy)₃]PF₆ in degassed ACN, $\Phi_{PL} = 9.5\%$. ¹⁷

The emission lifetime of the soft salt was recorded over different wavelength ranges: the first window (475-525 nm) is well suited to observe the blue Ir-based emission, while the second window (575-625 nm) was chosen to detect mainly the red Ru-based emission. In all cases except detection at 575-625 nm in 2-MeTHF, bi-exponential decay kinetics was obtained. An analysis of the two components evidenced the presence of a short decay, which corresponded well to the τ_e recorded in the same solvent for [2]Cl₂. The second long-lived component was tentatively assigned to the Ir emission, partially quenched by energy transfer to the acceptor. Notably, the Ir emission is much more strongly quenched as the polarity of the solvent decreases (Figure S7), in good agreement with the qualitative data obtained by steady-state measurements (Figure 3).

Conclusion. In conclusion, a three component soft salt containing an anionic iridium and a cationic ruthenium complex with complementary emission properties was synthesized and characterized by X-ray crystallography and different spectroscopic techniques. Particular attention was paid to the photophysical properties. The salt exhibited the luminescence features reminiscent of both photoactive ions. Changing the solvent or the concentration of the medium can easily modulate the relative emission intensities from the two components. In this manner, blue to orange-red emission, including near white emission could be observed. This mixed salt seems to have extremely interesting properties, pertinent in the field of white-light emitting materials.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, ¹H-NMR spectra, absorption and emission data, Stern-Volmer plot.

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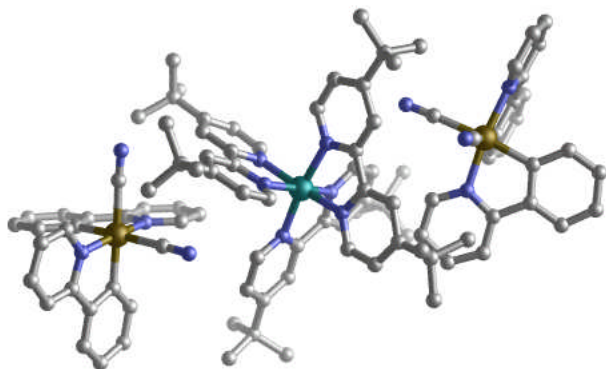
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TOC



We report the crystal structure and energy transfer behavior of a three component heterometallic soft salt composed of a blue-emitting anionic iridium complex and a red-emitting cationic ruthenium complex. The efficiency of the energy transfer can be modulated by changes in concentration and medium.