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COMMUNICATION

Enhanced Photophysics from Self-Assembled Cyclometalated Ir(III) Complexes in Water

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Two water-soluble anionic cyclometalated Ir(III) complexes, Ir(ppy)₂BPS [1] and Ir(F-mppy)₂BPS [2] have been synthesized and display clear evidence of self-assembly in water. Concentration-induced aggregation enhances the excited-state properties of both complexes, blue-shifting the photoluminescence emission energies as well as increasing the corresponding excited state lifetimes and quantum yields up to a factor of 5.

Over the last fifteen years, the library of luminescent Ir(III) complexes has expanded significantly.¹ Early synthetic efforts towards Ir(III) polypyridine complexes revealed the propensity of the iridium centre to spontaneously cyclometalate,² yielding molecules with large ligand-field stabilization energies and thereby enhanced thermal/photochemical stability as well as impressive emission tunability across the visible region of the spectrum.^{3,4,5,6} Consequently, such Ir(III) complexes have been studied for a variety of applications such as emitters in OLEDs,⁷⁻⁹ sensitizers in photochemical proton reduction reactions,¹⁰ and as chromophores for biological labelling^{4,11} and analyte sensing.^{12,13} However, the limited aqueous solubility of these complexes imposes severe restrictions on their utility in water-based applications, particularly solar fuels photochemistry.

A common approach for promoting the water solubility of transition metal complexes is the incorporation of appropriate solubilizing groups on the ligand framework.¹⁴⁻²⁰ Here, two anionic *bis*-cyclometalated Ir(III) chromophores have been studied, Ir(ppy)₂BPS [1] and Ir(F-mppy)₂BPS [2] (Fig.1), which utilize the commercially available bathophenanthroline disulfonate disodium salt (BPS) as the ancillary ligand. The ligand's peripheral sulfonate groups promote the solubility of the resulting complex. The excited-state properties of the

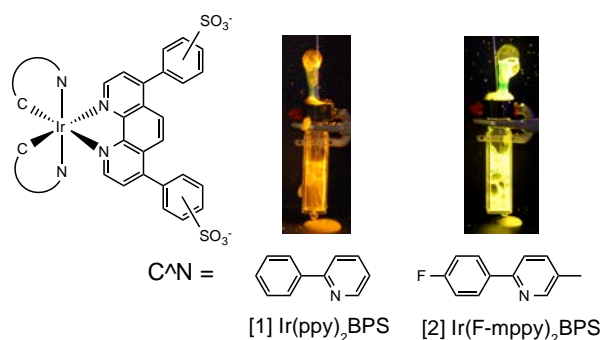


Fig. 1 Structures of 1 and 2 and photoluminescent bubbles formed during routine nitrogen sparging.

final desired molecule can be adjusted through modification of the cyclometalating ligand. Chromophore 2 incorporates the 2-(4-fluorophenyl)-5-methylpyridine (F-mppy) cyclometalating ligand, which has been shown to markedly improve the excited state lifetimes and quantum yields of the non-sulfonated derivative.¹⁰

To our surprise, upon nitrogen sparging aqueous solutions of 1 and 2, the immediate formation of photoluminescent bubbles visualized using 365 nm blacklight excitation was observed (Fig. 1). In fact, each dissolved chromophore can be completely removed from water as a soapy material using slow bubble degassing (Fig. S1). Further investigation into the aqueous behaviour of these complexes suggested a self-assembly process, occurring in water and scaling with concentration, which results in significant enhancements of the photophysical properties of 1 and 2.

It is particularly uncommon for aggregation to occur in octahedral transition metal complexes, as the molecular shape is not conducive to the formation of higher-ordered structures. Work by the DeCola group has shown that such complexes can form metallosurfactants through the incorporation of long alkyl chains, and has characterized the photophysical changes observed in these molecules upon aggregation.²¹⁻²⁴ The Bruce group has shown that through bulky, pro-mesogenic ligand substitutions, octahedral complexes can be made to form liquid crystalline phases.²⁵⁻²⁸ However, analogous

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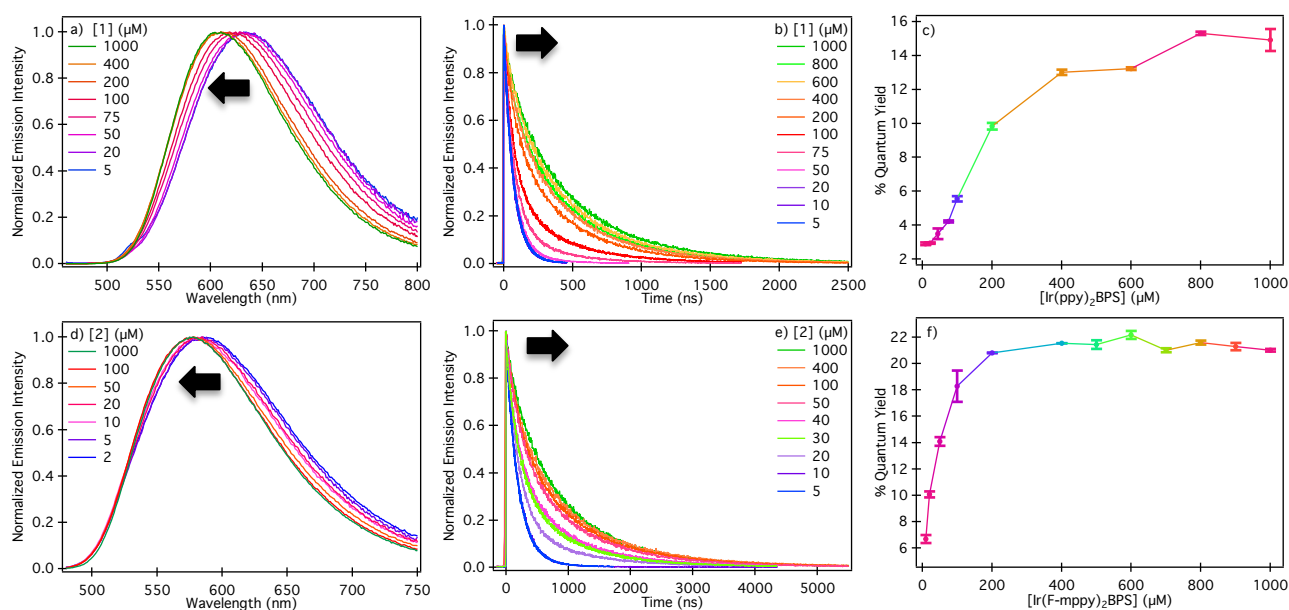


Fig 2 Concentration-dependent a) Emission of **1**, $\lambda_{\text{ex}} = 443$ nm b) Excited-state decays of **1**, $\lambda_{\text{ex}} = 405$ nm c) Quantum yields of **1** d) Emission of **2**, $\lambda_{\text{ex}} = 443$ nm e) Excited-state decays of **2**, $\lambda_{\text{ex}} = 405$ nm f) Quantum yields of **2**. All samples are contained in aerated water at the concentrations specified in the legends.

molecular features are noticeably lacking in **1** and **2**. Here we describe the unexpected self-assembly phenomenon that is observed in aqueous solutions of **1** and **2** and characterize the resultant effects on their photophysical properties.

The UV-vis absorption spectra of **1** and **2** (Fig. S2) are representative of *bis*-cyclometalated diimine Ir(III) complexes. Based on comparisons with the literature,^{29–32} the high-energy transitions below 320 nm are assigned to spin allowed π – π^* transitions localized on the cyclometalating and diimine ligands. Due to the anionic charge of the cyclometalating carbon, these ligand-centred (LC) transitions are expected to occur at higher energy than those of the ancillary ligand.³³ At lower energy, we observe less intense overlapping bands attributed to spin allowed metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT) transitions. The lowest intensity bands above 430 nm have been assigned to spin-forbidden charge transfer (CT) transitions, which gain intensity through the large spin-orbit coupling constant of the iridium centre. No changes in the absorption profile were observed with increasing concentration, and no Mie scattering was detected at any concentrations investigated.

Both molecules display broad, unstructured photoluminescence profiles in solution, consistent with the dominant CT character of their emissive excited states. The HOMO for these complexes contains contributions from the Ir(III) metal orbitals as well as from the cyclometalating ligand, whereas the LUMO is centred on the ancillary BPS ligand, making the lowest energy transition a mixture of MLCT/LLCT.¹⁴ The emission of CT type complexes is particularly sensitive to

solvent/environment polarity,³⁴ which is observed in **1** and **2** through solvatochromic shifting of their emission energies in organic solvents of differing polarity (Fig. S3).

In water, the emission energy of both complexes displayed strong concentration dependence (Fig. 2). A discrete shifting of the photoluminescence profiles towards higher energy was observed as the aqueous concentration was increased in the range of 20–400 μM for **1** (629 to 610 nm, 495 cm^{-1}) and 2–100 μM for **2** (585 to 578 nm, 207 cm^{-1}). These blue shifts indicate a self-assembly process that renders the immediate chromophore domain less polar than the solvated water environment. Similar shifts in Ir(III) emission energies have been reported in the formation of aggregates by metallosurfactants²² and metallomesogens.³⁵ In organic solvents, the emission energy does not change with concentration, consistent with molecularly derived photophysics.

Further evidence of aqueous self-assembly was observed in the time-resolved photoluminescence intensity decays of **1** and **2** (Fig. 2). In dilute solution ($\leq 20\text{ }\mu\text{M}$ for **1** and $\leq 10\text{ }\mu\text{M}$ for **2**), the decays were concentration-independent and were adequately fit with single exponential functions. Above these concentrations, the decay profiles systematically lengthen with increasing concentration. From 50–100 μM for **1** and 20–40 μM for **2** the resultant fits become biexponential, suggesting the presence of two (or a narrow distribution of two) distinct chromophore environments. Further increases in the concentration beyond this range produces excited state decays

| Complex | Concentration (μM) | Φ_{Em} (%) ^a | Average Lifetime (ns) ^b | k_r ($\times 10^5 \text{ s}^{-1}$) | k_{nr} ($\times 10^5 \text{ s}^{-1}$) |
|----------|---------------------------------|-------------------------------------|------------------------------------|--|--|
| 1 | 10 | 2.9 | 69 ^c | 4.19 | 140.4 |
| | 50 | 3.2 | 106 ^d | 3.00 | 91.4 |
| | 100 | 5.5 | 234 ^d | 2.37 | 40.3 |
| | 400 | 13 | 306 ^e | 4.26 | 28.5 |
| | 1000 | 14.9 | 353 ^e | 4.23 | 24.1 |
| 2 | 10 | 6.7 | 211 ^c | 3.18 | 44.2 |
| | 50 | 14.0 | 338 ^e | 4.17 | 25.4 |
| | 100 | 18.3 | 432 ^e | 4.24 | 18.9 |
| | 400 | 21.6 | 654 ^e | 3.30 | 12.0 |
| | 1000 | 21.0 | 665 ^e | 3.16 | 11.9 |

Table 1 Concentration-dependent photophysical properties of **1** and **2** in air-equilibrated water. ^aAverage of 2 relative quantum yield measurements accurate to $\pm 1\%$. ^bAverage of two time-resolved emission experiments, all lifetimes within ± 13 ns. ^cMonoexponential decay. ^dBiexponential decay, average lifetime, $\langle \tau \rangle = \sum \alpha_i \tau_i^2 / \sum \alpha_i \tau_i$. ^eStretched exponential decay, average lifetime, $\langle \tau \rangle = (\tau/\beta)\Gamma(1/\beta)$.

that are best fit using a stretched exponential function $I(t) = I_0 \exp(-kt)^\beta$,³⁶ suggesting a heterogeneous chromophore environment modelled by a distribution of excited state lifetimes. The width of the distribution (effectively the heterogeneity of the environment) is given by the fitting parameter β . For both complexes this value is smaller for the lower concentrations in this fitting regime and approaches unity (less heterogeneity) as the concentration is increased to 1 mM, where the observed lifetime enhancements level off. These data appear to indicate the complexity of the self-assembled soft materials produced in each case. In organic solvents the intensity decays remain constant and single exponential over the same concentration range in both **1** and **2** (Fig. S4).

Similar to the trend observed in excited-state lifetimes, the quantum yields calculated for both complexes show significant enhancement with increasing concentration in water (Fig. 2). The quantum yield of **1** increased by a factor of 5, from 3 to 15%, while that of **2** increased from 7 to 21% on going from 10 μM to 1 mM. Likely, a combination of factors contributes to these quantum efficiency enhancements, which are summarized in Table 1. As the photoluminescence energy increases with concentration, the lifetimes and quantum yields would also be expected to increase as a consequence of the energy gap law. Complex **1** shows the greatest degree of emission blue shifting with concentration, and also possesses the greatest total enhancement in lifetime and quantum yield. It has also been suggested that self-assembled structures can protect the excited chromophore from quenching by diffusing oxygen in air-equilibrated samples.²³ At a concentration of 1 mM, a minimal improvement in lifetime is observed between air-equilibrated and air-free samples of **1** despite an average lifetime of 353 ns, suggesting that the aggregate is quite effective at protecting the long-lived triplet excited state from oxygen quenching (Fig. S4). Additionally, the more rigid aggregate environment can potentially suppress non-radiative

decay pathways, further contributing to improvements in lifetime and quantum yield.²³ Table 1 indicates that the radiative rate constants for **1** and **2** are essentially constant over the concentration range measured, however the non-radiative decay rates show a significant decrease as the concentration increases. In air-equilibrated solutions, this rate constant would include contributions from oxygen quenching as well as a more rigid environment.

Similar photophysical enhancements are observed in aqueous solutions of **1** and **2** upon addition of salt. A 20 μM solution of **1** shows a lengthening of excited-state decay profiles as well as enhancement in quantum yield from 3 to 12% in solutions of sodium chloride up to 1.0 M. A 10 μM solution of **2** displays similar behaviour, with quantum yields increasing from 7 to 16% (Fig. S5). This effect was also observed by the additions of either potassium chloride or potassium nitrate (Fig. S6). Salt effects are well known in ionic surfactants, where the addition of salt lowers the CMC by shielding the charged molecules from repulsive interactions, facilitating aggregate formation at lower concentrations.³⁷ While we believe a similar mechanism is responsible for the photophysical enhancements observed in **1** and **2** upon addition of salt, we were unable to measure any changes in the surface tension of aqueous solutions with increasing Ir(III) concentration, indicating that these complexes are not surfactant-like.

Dynamic light scattering (DLS) measurements were used to estimate the size of aggregates in aqueous solution (Fig S7). At a concentration of 1 mM, solutions of **1** indicate particles with a hydrodynamic radius of 2 nm, and **2** indicate a radius of 5 nm. Both complexes also show a polydisperse peak in the data around a radius of 100 nm, however, as larger particles scatter more light, these peaks are overrepresented in the present scattering data. It is likely that the aqueous compositions contain mostly smaller particles in solution, consistent with the lack of Mie scattering observed by UV-Vis experiments.

Cryo-SEM images confirm the formation of smaller aggregates in 1 mM aqueous solutions of **1** (Fig. 3). Attempts to image aggregates using drop-cast methods were unsuccessful; the ability to measure samples in solution was imperative. While these images represent aggregates in frozen solution, the size distribution agrees reasonably well with that obtained by DLS for **1** in liquid water, indicating an average aggregate radius of 7 nm.

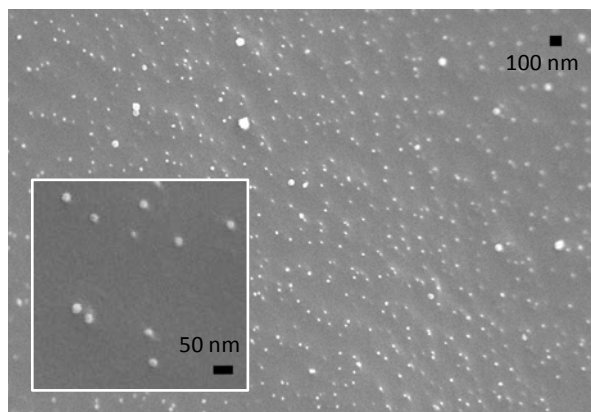


Fig. 3 CryoSEM images of **1** (1 mM) in frozen aqueous solution.

In conclusion, Ir(III) chromophores **1** and **2** were rendered water-soluble by the incorporation of peripheral sulfonate groups on the diimine ancillary ligand. Both octahedral molecules were shown to form concentration-dependent aggregates in aqueous solution, without the need for structurally complex ligands to induce self-assembly. Work is currently underway to further understand the driving forces behind the aggregation behaviour observed in **1** and **2**. In the future, this unusual self-assembly phenomenon can potentially be exploited in solar fuels photochemistry, where increased photosensitizer concentration renders the composition more reactive than its molecular counterpart.

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