New ionic dinuclear Ir(III) Schiff base complexes with aggregation-induced phosphorescent emission (AIPE)

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Solid-state organic luminescent materials are of interest for both fundamental studies and practical applications due to their important roles in such diverse areas as solid-state light-emitting electrochemical cells (LECs),

chemosensors,

photocatalysts for hydrogen generation,

and biochemical probes.

In this regard understanding and controlling intermolecular interactions is a key topic, as aggregate formation – both in solution and in the solid-state – often quenches light emission.

In 2002, Park et al.

reported an important class of compounds which display aggregation-induced emission (AIE); they emit weakly when dispersed and show strong emission when aggregated or in the solid state. In 2002, Park et al.

reported aggregation-induced enhanced emission (AIEE) in similar materials. Since then, AIE and AIEE have attracted considerable attention for potential applications in fields such as organic light-emitting devices (OLEDs), bioelectronics and chemosensors.

It is generally agreed that AIE occurs when molecular packing leads to restricted molecular rotation or torsion which blocks non-radiative channels and effectively suppresses self-quenching. To date only a few neutral iridium complexes with aggregation induced phosphorescent emission (AIPE) have been well studied.

In 2010, Youngkyu Do et al.

reported a neutral dinuclear iridium(III) complex which showed AIE character. In 2012, our group

reported the first ionic mono-nuclear Ir(III) complex which displayed AIE.

However, AIPE materials with high quantum yield are still rare,

especially ionic transition metal complexes. In this regard, dinuclear Ir(III) complexes are promising candidates. Recently, a series of dinuclear iridium(III) complexes were exploited in LECs.

It is clear that the nature of the bridging atoms or ligand(s) in dinuclear complexes plays a fundamental role in adjusting the luminescence properties.

Compared with the typical N,N-chelating ligands, such as 2,2′-bipyridine and 1,10-phenanthroline, Schiff base ligands are structurally versatile and can act as both chelating and bridging motifs. The flexible nature of the diimine spacer allows the ligand to bend and rotate freely when coordinating to metal centres so as to adopt the optimum coordination geometries of the metal ions. The motivation for the present work is to study dinuclear iridium complexes with bridging diimine ligands that are able to electronically couple the two metal centres and offer the potential for AIPE.

The complexes 1 and 2 (Scheme 1 and Scheme S1, ESI†) were prepared by the standard procedure in high yield. The Schiff-based ligands were synthesised following a previous method (Scheme S1, ESI†). The complexes are only very weakly emissive in solution, whereas they are brightly luminescent in solid thin films. Thus, to our knowledge, 1 and 2 present the first examples of ionic dinuclear Ir complexes with AIPE. The crystallographic analysis of

![Scheme 1 Chemical structures of the complexes, with bridging phenyl (1) and biphenyl (2) units.](image_url)
the complexes and density functional theory (DFT) gives insight into the origin of their luminescence.

Noncovalent intra- and intermolecular effects in single crystals can be used to interpret the origin of the enhanced emission. The X-ray molecular structure of complex 2 is shown in Fig. 1(a). (For complex 1, see ESI† Fig. S5). Complex 2 has distorted octahedral geometry around the two Ir centres, which are coordinated by four cyclometalated ligands (CN, ppy) and one ancillary ligand (N,N-), adopting C,N-coordinated by four cyclometalated ligands (C,N, ppy) and one distorted octahedral geometry around the two Ir centres, which are

![Image](image_url)

**Table 1** Photophysical data for complexes 1 and 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_{abs} (nm)</th>
<th>λ_{em} (nm)</th>
<th>Φ_L</th>
<th>τ (ns)</th>
<th>k_{n} (×10^{9} s^{-1})</th>
<th>k_{nr} (×10^{7} s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>252, 369</td>
<td>644</td>
<td>0.373</td>
<td>47.66</td>
<td>7.83</td>
<td>1.32</td>
</tr>
<tr>
<td>2</td>
<td>254, 376</td>
<td>692</td>
<td>0.264</td>
<td>38.68</td>
<td>6.83</td>
<td>1.90</td>
</tr>
</tbody>
</table>

a Measured in CH$_3$CN (1.0 × 10^{-3} M) at room temperature. b Measured in the film state at room temperature; τ_{exc} = 370 ns; error for Φ_L ± 5%. The radiative k_{r} and non-radiative k_{nr} values in neat film were calculated according to the equations: k_{r} = Φ/τ and k_{nr} = (1 - Φ)/τ, from the quantum yields Φ and the lifetime τ values.

![Image](image_url)

**Fig. 2** (a) UV-Vis absorption and emission spectra of complexes 1 and 2 (1 × 10^{-5} M) in CH$_3$CN solution at room temperature. (b) Emission spectra of complex 1 in CH$_3$CN–water mixtures with different water fractions (0–90% v/v) at room temperature.
on the two iridium centres and four cyclometalated ppy ligands, whereas in solution only one iridium centre and two cyclometalated ppy ligands participate in the HOMO of 2 (Fig. 4). These results indicate that much more efficient electronic interaction can be induced between the Ir-centred moieties and the bridging ligand in the solid state than in the solution state of 2 due to the planar geometry of the bridge in the solid. For complex 1 with a phenyl bridge, the HOMO is similar in both the solution and solid states (Fig. 4). The HOMO and LUMO energy levels in solution and solid states are shown in Fig. 4. The energy levels are lowered in the solid state, probably due to intramolecular or intermolecular interactions.

The emitting triplet states for 1 and 2 are shown to be a mixture of metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT) transitions (Fig. S15, ESI†). Nonetheless, another important feature should be considered. Table S5 (ESI†) lists the selected calculated bond lengths, bond angles and dihedral angles at both the optimized ground state (S0) and triplet excited state (T1) for 1 and 2. Structural distortions are found in the T1 geometry compared to the S0 geometry in both complexes which induce a larger excited-state relaxation and may result in an effective pathway for nonradiative decay.

In summary, two new ionic dinuclear Ir(n) Schiff base complexes with unusually high PLQY in neat thin films have been studied. X-ray crystal structure analysis and TD-DFT calculations suggest that restricted intramolecular relaxation in the solid state leads to the observed AIPE. This should be a versatile strategy for obtaining highly efficient ITMCs for future applications.

The work in China was funded by NSFC (51203017 and 21303012), the Science and Technology Development Planning of Jilin Province (20100540 and 20130522167[J]).

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