**ARTICLE**

**[Ag(IPr)(bpy)][PF$_6$]: Brightness and Darkness Playing with Aggregation Induced Phosphorescence for Light-emitting Electrochemical Cells**

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Heteroleptic silver(I) complexes have recently started to attract the attention in thin-film lighting technologies as an alternative to copper(I) analogous due to lack of flattening distortion upon excitation. However, the interpretation of their photophysical behavior is challenging going from traditional fluorescence/phosphorescence to a temperature-dependent dual emission mechanism and to a ligand-lock assisted thermally activated delay fluorescence. Herein, we unveil the photoluminescence behavior of a three-coordinated Ag(I) complex with N-heterocyclic carbene (NHC) ligand and 2,2'-bipyridine (bpy) as N,N ligand. In contrast to its low-emissive Cu(I) complex structural analogous, a strong greenish emission was attributed to the presence of aggregates formed by π-π intermolecular interactions as revealed by the X-ray structure and aggregation induced emission (AIE) studies in solution. In addition, the temperature-dependent time-resolved spectroscopic and computational studies demonstrated that the emission mechanism is related to a dual photophysics emission mechanism of two very close lying (ΔE = 0.08 eV) excited triplet states, exhibiting a similar delocalized nature over the bipyridine ligands. Unfortunately, this favourable AIE is lost upon forming homogenous thin-films suitable for lighting devices. Though the films showed a very poor emission, the electrochemical stability under device operation conditions is remarkable compared to the prior-art, highlighting the interest of [Ag(NHC)(N,N)] [X] complexes for thin-film lighting.

**Introduction**

Known since the ancient times, coinage metals have always played an important role in every-day life. Recently, modern chemistry fueled more sophisticated uses of d$^{10}$-metal derivatives. They have been widely exploited as catalysts, while they have become more and more attractive for the replacement of rare and expensive metal components, such as Ir(III), Ru(II) and Pt(II)-based compounds, in optoelectronics.

In this context, the primacy of heteroleptic Cu(I)-complexes combining diimine (N,N) and diporphine (P,P) ligands ((Cu(N,N)(P,P))$^+$) for thin-film, solid-state lighting (i.e., light-emitting electrochemical cells or LECs and organic light-emitting diodes or OLEDs) and photovoltaics (i.e., solar sensitized solar cells or DSSCs) has been heralded owing to their well-established chemistry to tune photophysical and electrochemical features, and their highly efficient emission mechanism via thermally activated delayed fluorescence (TADF); the ability to harvest both singlet and triplet excitons, leading to virtual lighting device efficiencies of 100%.

Conversely, the chemistry and the photophysical and electrochemical behaviors of their homologous Ag(I) complexes ([Ag(N,N)(P,P)]$^+$) have attracted much less attention. However, research interest in silver(I) complexes is back with the promise to overcome the limitations of their copper(I) homologues arising from their labile coordination sphere. In short, their emitting excited state features a strong metal-to-ligand charge transfer (MLCT) character, in which the metal ion center is formally oxidized (d$^9$ configuration), leading to a square-planar coordination geometry. This flattening distortion causes unforeseen changes in the emission features going from powder to solution and to thin-films applied to devices. A reduction of the photoluminescence quantum yield (Φ), and better accessibility of nucleophiles, like solvent molecules, forming non-emissive species during device fabrication. In stark contrast, the 4d orbitals of the silver metal center are lower in energy compared to those related to the ligands. Thus, Ag(I) complexes are usually characterized by ligand-centered (LC) emitting excited states with a small MLCT contribution. While this usually results in higher stabilities due to the lack of flattening distortion upon excitation, the emission mechanism is difficult to predict even for similar heteroleptic [Ag(N,N)(P,P)]$^+$. Indeed, more and more...

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**Footnotes:**

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Finally, this complex also exhibits a stable electrochemical behavior without showing the formation of Ag(0)-nanoclusters upon electrochemical stress. Thus, they were implemented into LECs that showed the expected ion-assisted electrical behavior with a remarkable electrochemical stability, but no light response, since the lack of aggregation in the desired smooth and homogenous active layers leads to the formation of non-emissive excitons. All in all, this work highlights our strive on the aggregation dilemma as a key to design bright Ag(I)-based complexes that, unfortunately, leads to dark thin-film lighting devices with a remarkable electrochemical stability.

Results and Discussion

Synthesis and Structural Characterization

At first, IPr (IPr = 1,3-bis(2,6-di-iso-propylphenyl)imidazol-2-ylidene) was selected as NHC ligand for its well-known steric and σ-donation properties and their wide use in copper congeners. Then, following the procedure reported by Nolan and co-workers, the [AgCl(IPr)] precursor was prepared in 88% isolated yield. The archetypal [Ag(IPr)(bpy)][PF$_6$] was synthesized using our previously reported procedure for analogous Cu(I) complexes. In detail, a mixture of 1 eq. of [AgCl(IPr)] with 1.05 eq. of 2,2'-bipyridine (bpy) was heated up to 78 °C in EtOH for 1 h. Precipitation with a saturated aqueous solution of KPF$_6$ (10 eq.) furnished the expected complex. $^1$H NMR analysis of the crude reaction showed the presence of 10% of the homoleptic complex [Ag(IPr)$_2$][PF$_6$]. However, two consecutive slow gas-diffusion recrystallizations, from a dichloromethane solution of the crude silver complex using diethyl ether as light solvent, furnished the pure complex [Ag(IPr)(bpy)][PF$_6$] in 52% isolated yield as suggested by NMR spectroscopy. The coordination of the NHC ligand was confirmed by $^{13}$C NMR spectroscopy with the presence of the typical two doublets centered at 186.2 ppm, resulting from the coupling between the carbenic carbon and the two magnetically active isotopes of silver ($^{107}$Ag and $^{109}$Ag).

Fig. 2 (A) Ellipsoid representation at 50% probability from the X-ray diffraction analysis of [Ag(IPr)(bpy)][PF$_6$]; 2 molecules of [Ag(IPr)(bpy)][PF$_6$] in the crystal cells exhibiting π-π interaction between bpy ligands. In the picture are graphically defined: the ring-centroid vector (red), vector normal to the ring (blue), the displacement angle (green). (B) One molecule of [Ag(IPr)(bpy)][PF$_6$] showing no CH-π interaction between bpy and IPr ligands. Anion and some hydrogen atoms are omitted for clarity.
Next, suitable single crystals were grown from a concentrated CH$_2$Cl$_2$ solution using slow gas-diffusion technique with diethyl ether as light solvent. X-ray diffraction analysis was conducted to unambiguously prove the structure. The most relevant values of bond lengths and angles are reported in Table 1 and Figure 2, while all the structural values and experimental details are provided in the experimental part and in Supporting Information – Table S1. In short, the 2,2'-bipyridine ligand and the Ag(I) metal centre formed the expected five-membered chelating ring. With the additional IPr ligand, the expected trigonal geometry for such complex was also proven – Figure 2. Then, the Ag-C bond length was measured at 2.0723(12) Å and the two Ag-N bonds at 2.2928(11) and 2.2944(11) Å, in line with data from the literature. The bite angle of the N-N ligands toward the metal center was found at 71.86(4)° which was smaller by around 10° than in the copper analogue reported previously (80.04(7)°). The distances between the hydrogen atoms in α position of the nitrogen atoms in the 2,2'-bipyridine and the centroid of the N-substituted aromatic rings of the NHC (CH··C$_g$) was estimated over 3 Å, resulting in the loss of the CH··π interaction that was observed in the copper(I) complexes. Nevertheless, long-range intermolecular π··π interactions occurred between the pyridines of the bpy ligand with centroid-centroid (C$_g$··C$_g$) distances of 3.82 Å and displacement, defined as the angle between the centroid-ring vector and the ring normal, of 21.3° – Figure 2.

**Photophysical and Computational Studies**

The most relevant photophysical figures are summarized in Table 2. The UV-Vis absorption features in diluted solution (10$^{-5}$ M in THF) show the typical two structured bands centred at ca. 250 and 290 nm that are assigned to π··π* ligand-centred transitions – Figure 3A, while a very weak (φ < 1%) and structured emission centred at 365 nm is associated to very short excited state lifetimes (τ) in the ns regime. Thus, this emission mechanism is attributed to a ligand-centered fluorescence. In stark contrast, the crystalline powder features a broad emission band centred at 500 nm – Figure 3B, representing a significant wavelength shift of around 150 nm that is associated to φ and τ values of 18% and 571 μs, respectively. This could be attributed to a change of the nature of the excited state going from solution to crystalline powder caused by the intermolecular π··π interactions described above. To investigate the presence of aggregation induced emission (AIE) phenomena, we simple force the aggregation phenomena in THF solution (10$^{-5}$ M) by adding different volume ratios of distilled water ($f_w$) – Figure 3C. Upon increasing the $f_w$ to 70% (v/v), a new low-energy emission band centred at 500 nm start evolving, while a broad and intense emission similar to that of crystalline powder was finally noted at $f_w$ = 90%.

Interestingly, emission band shape as well as φ and τ values nicely match with those noted for powder – Table 2.
The τ vs. T plot that follows a Boltzmann-type distribution described by Equation 1 – Figure 4B: 

\[ \tau_{em}(T) = \frac{1 + e^{\frac{-\Delta E(T_{1A} - T_{1B})}{k_B T}}}{\frac{1}{\tau(T_{1A})} + \frac{1}{\tau(T_{1B})} e^{\frac{-\Delta E(T_{1A} - T_{1B})}{k_B T}}} \]

where \(k_B\) is the Boltzmann constant, \(\Delta E(T_{1A} - T_{1B})\) is the energy gap between the two excited states and \(\tau(T_{1A})\) and \(\tau(T_{1B})\) are the excited state decay lifetimes of the respective triplet excited states. This fitting indicates the presence of a temperature-equilibrated dual phosphorescence mechanism from two triplet excited states, namely \(T_{1A}\) and \(T_{1B}\), with a triplet-triplet energy splitting of \(\Delta E(T_{1A} - T_{1B}) = 0.08 \text{ eV}\). To get more insights into the nature of these triplet excited states, they were modelled using density functional theory (DFT) and its time-dependent version (TD-DFT) methodology – see experimental section; Tables S2-S4 and Figure S6. This confirmed the presence of two low-lying triplet equilibrium structures where the triplet states are delocalized over the two bipyridine ligands – see Supporting Information. In line with the experimental data, these states exhibit a very small energy difference (adiabatic \(\Delta E(T_{1A} - T_{1B}) = 0.008 \text{ eV}\)), while the calculated singlet excited states are not thermally accessible with a singlet-triplet energy gap of ca. 0.88 \text{ eV}. Finally, vertical energy differences \((T_{1A}/S_0)\) of 2.60 \text{ eV} (477 \text{ nm}) and 2.58 \text{ eV} (481 \text{ nm}) were found for \(T_{1A}\) and \(T_{1B}\), respectively – Tables S2-4, supporting the assignment of the emission mechanism to a thermally equilibrated dual-phosphorescence.

Fig. 4 (A) Emission spectra of [Ag(IPr)(bpy)][PF₆] in powder at different temperatures – see legend. (B) τ vs. T plot along the fitted equation 1 (red).
from 15 mg/ml acetonitrile solutions, forming homogenous films with no visual aggregates and a roughness below 1 nm – Figure 5A. In contrast with the photoluminescence in solution and powder, the emission of the films consists of a broad band centered at 540 nm (i.e., 40 nm red-shifted) and exhibits a dramatic reduction of the ϕ and τ values (i.e., < 2.0 % and 133 μs; Table 2 and Figure 5A). This is typically ascribed to aggregation induced quenching phenomena occurring upon film forming.36 Here, the formation of aggregates induced by the quick drying of the solvent upon spinning as well as the presence of solvent molecules leads to a non-emissive species, in which short- and long-range intermolecular interactions are different to those noted in their X-ray structures. Indeed, drop-casted films formed by a slow evaporation under ambient conditions led to non-homogenous films with the same photoluminescence features similar to those in powder – Table 2 and Figure 5B. Though aggregation is the key to unlock the photoluminescence features of [Ag(IPr)(bpy)][PF₆], our efforts changing thin-film forming conditions (spinning/blading, solvents, and additives, such as ionic liquids and polymers) did not lead to simultaneously meet good film quality for devices and photoluminescence features similar to those in powder.

**Preparation and characterization of LECs**

Despite the poor photoluminescence features in thin-films, we decided to study the electroluminescent behavior in LECs. In short, a layer (70 nm) of poly(3,4-ethylene dioxythiophene) :polystyrene sulfonate (PEDOT:PSS) was spin-coated onto a clean indium-tin-oxide (ITO) electrode-coated glass to increase reproducibility. Then, the active layer (ca. 90 nm) was deposited via spin-coatings as above explained. Finally, 100 nm of the aluminum cathode was deposited via physical vapour deposition to finalize the devices’ architecture. The devices were driven at pulsed current of 8 mA, using a 1 kHz block-wave and 50% duty cycle on 10 mm² pixels. Unfortunately, all the devices did not light up as expected by the poor photophysical features in thin-film, but showed a stable electrical behavior compared to that of the prior-art – Figure 6A.22,28,44 In detail, the average voltage reduces exponentially until a stable plateau is reached. This is related to the formation of electrical double layers (EDL) at the electrode interface by the drifting of ions upon applying an external electrical field. The second stage is achieved once the ohmic contacts are formed. Here,
charge injection is stable and the doped regions are slowly growing until a stable p-i-n junction is formed. This is typically affected by the electrochemical degradation of the oxidized/reduced species that leads to unforeseen changes in the average voltage profile over time that either increases caused by the formation of carrier trappers, (e.g., Cu(II) species in the case of Cu(I)-based devices) or decreases caused by the formation of highly conductive degradative compounds, such as Ag(0) nanostructures. Since the voltage profile is stable, we can infer that electrochemical degradation of [Ag(IPr)(bpy)][PF$_6$] in thin-films is not happening. Electrochemical Impedance Spectroscopy (EIS) assays were performed to deeper investigate the electrical behavior using a single resistor/capacitor equivalent circuit to analyse the dominant processes upon increasing the applied voltage – Figure 57. Thus, the device resistance profile is characterized by i) an exponential decrease during the formation of the EDLs at low applied voltages before carrier injection occurs and ii) a linear regime related to a balanced growth of the p- and n-regions at voltages above the electrochemical band-gap of the complex. The representative values calculated at 0 V are dielectric constant ($\varepsilon_r$) and ionic conductivity ($\sigma$) that are 13.95 and 8.08×10$^{-8}$ S m$^{-1}$, respectively. While the $\varepsilon_r$ is high compared with other thin-films with similar d$_{15}$-complexes, $\sigma$ values are two-order of magnitude lower, indicating that the growing of the doped regions must be slower than in analogous complexes. However, the most relevant feature is the lack of meaningful changes in the resistance profile of the device upon comparing both, fresh and used devices – Figure 6. This nicely confirms that the electrochemical stability of [Ag(IPr)(bpy)][PF$_6$] thin-films is remarkable.

Conclusions

This work highlights the bright and dark sides of a unique aggregation induced emission (AIE) in archetypical tri-coordinate [Ag(IPr)(bpy)][PF$_6$] complexes. Intermolecular π–π interactions determined in the X-ray structures have a pivotal role in the photophysical behavior of the complex that show remarkable $\Phi$ values of 20 %. What is more, temperature-dependent lifetime measurement revealed the presence of a dual phosphorescence behavior related to two triplet excited states thermally interconnected (ΔE of 0.08 eV). This was further supported by computational studies that determine the presence of two very close lying excited triplet states (adiabatic ΔE of 0.008 eV) with a similar delocalized nature over the bipyrindine ligands. Unfortunately, this favorable AIE is lost upon forming homogenous thin-films suitable for lighting devices. Here, films feature a very poor emission with $\Phi$ < 2 % that leads to dark LECs. However, the electrical behavior of the device is outstanding compared to that of devices with tetragonal heteroleptic Ag(I) complexes, since the formation of Ag(0) nanocluster is not observed by electrochemical impedance spectroscopy. Finally, the photophysical characteristics and the stability of [Ag(IPr)(bpy)][PF$_6$] open up new possibility of exploration of new [Ag(NHC)(N=N)]X complexes, seeking the optimization of the AIE behavior upon device fabrication.

Experimental part

General considerations

Synthesis. All the commercially available compounds were purchased and used without further purification. All the reactions were performed under dry argon atmosphere, using standard Schlenk technique. Purchased sorbents were degassed bubbling Ar directly in bulk. Details about the synthesis and the characterization of [Ag(IPr)(bpy)][PF$_6$] are provided in the Supporting Information.

Crystallography. Crystallographic data sets were collected from single-crystal samples, performing the analysis with a Bruker Kappa APEXII CCD diffractometer. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 6.0° scan in 12 frames over three different parts of the reciprocal space (36 frames total). Cell refinement and data reduction were performed with SAINT (Bruker AXS). Absorption correction was done by a multiscan method using SADABS 2012/1 (Bruker AXS). The structure was solved by direct method and refined using SHEXL-97 or SHEXL-2013 (Sheldrick). All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters while hydrogen atoms were placed in idealized positions. The short interactions were calculated using the software Platon version 250420.

Photophysical measurements. UV-Vis absorption spectra in solution were collected at room temperature with a Shimadzu UV/2600i spectrometer. Steady-state emission spectra and $\Phi$ were measured with FSS Spectrofluorometer (Edinburgh Instruments) equipped with integrating sphere. The measurements of the time-resolved photoluminescence were performed using Multi-Channel Scaling (MCS) as photocounting method and pulsed μs Xe-flash lamp as excitation source (Edinburgh Instruments, FSS Spectrofluorometer). For temperature-dependent measurements, the FSS Spectrofluorometer (SC-80 holder) was equipped with an optical cryostat (Optistat-DN, Oxford Instruments). The intensity-weighted intensity lifetime was used in the case of biexponential decays of the excited state. Thin-film for optical characterization were prepared spin-coating the complex filtered solution (15 mg/ml in acetonitrile, thickness: 90 nm) onto clean quartz slides. The AFM of the resulting samples was performed with MFP-3D Origin+ Oxford Instruments to confirm the suitable morphology of the layers.

Theoretical details. The relaxed structures of the lowest-lying triplet states were obtained using a [Ag(IPr)(bpy)][PF$_6$] dimer obtained from the X-ray resolved structure. Geometry relaxation was carried out using linear response time-dependent density functional theory (TDDFT)$^{64}$ employing the CAM-B3LYP exchange-correlation potential$^{65}$ and the def2-TZVP basis set.$^{66}$ Dispersion interactions were accounted for using the dispersion correction of Grimme and co-workers including the Becke-Johnson damping.$^{67,68}$ The core electrons of Ag were
Spin-orbit coupling TD-DFT calculations including 20 singlet and 20 triplet states were carried out on the relaxed structures using the zero-order regular approximation (ZORA) Hamiltonian,\textsuperscript{72,73} the CAM-B3LYP exchange-correlation functional, and the ZORA recontracted def2-TZVP and SARC-ZORA-TZVP basis set for Ag\textsuperscript{74} as implemented in ORCA 5.0.3.\textsuperscript{75,76} The corresponding Coulomb fitting auxiliary basis sets were used.\textsuperscript{77,78} The spin-orbit integrals were calculated using the RI-SOMF(1X) approximation.\textsuperscript{79}

Device preparation and characterization. Narajo Substrates provided ITO (130 nm) substrates. The cleaning of the substrate is composed to four steps: water diluted Derquim\textsuperscript{®} detergent (ratio 1:1), distilled water, ethanol and propan-2-ol as solvents in a warm ultrasonic bath (60°C, 37-70 Hz) for 15 min each step. Then, the substrates were dried in N2 flow and treated in a UV ozone cleaner for 8 min. The aqueous PEDOT:PSS (Clevios P VP.Al4083) was diluted with propan-2-ol (ratio 3:1). The corresponding Coulomb fitting auxiliary basis sets were used. The resulting solution was sonicated for 10 min and then filtered (0.45 μm pores diameter) before the spin-coating onto the clean ITO substrates. The resulting layers were dried on a heating plate at 120°C and stored in the glovebox (N2 atmosphere, < 0.1 ppm O2 and H2O, Ångstrom Engineering). The complex was dissolved in acetonitrile, reaching the concentration of 15 mg/ml. The solution was sonicated for 10 min and then filtered (0.45 μm pores diameter) before the spin-coating onto the active layer via physical vapor deposition (Ångstrom Covap evaporator integrated in the glovebox, < 1×10\textsuperscript{-6} mbar). A shadow mask was used to define pixels with an area 10 mm\textsuperscript{2}. Voltage and current performances of the devices were evaluated with Botest OLT OLED Lifetime-Test System operating in pulsed mode. Metrohm \textmu{}Autolab III circuit model reported in the Supporting Information – s18.

Conflicts of interest
There are no conflicts to declare.

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Notes and references