## Remarkable Mg<sup>2+</sup>-selective emission of an azacrown receptor based on Ir(III) complex<sup>†</sup>

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A new aza-15-crown-5 ether-appended iridium complex was synthesized and showed promising *on-off* selective emission-triggering by inhibition of photoinduced electron transfer (PET) upon binding of  $Mg^{2+}$ .

Selective sensing of metal ions plays a crucial role in fields as diverse as chemistry, biology, environmental and material sciences. The ionophore-luminophore approach has become of particular interest to design chemosensors as a convenient and high-sensitivity strategy. Transition metal complexes such as platinum(II), ruthenium(II) or rhenium(I) proved to have many advantages as luminophores (large Stokes shift, long excited-state lifetime) compared to organic emitters. Recently, iridium complexes emerged as especially suitable candidates in the design of new chemosensors, luminescent biological labels, OLEDs, or molecular switches due to their exceptional luminescent properties and the possibility to fine-tune these properties by ligand substitution.<sup>1,2</sup> The aza-crown ether motif is of particular interest as an ionophore due to its on-off luminescence switching upon cation binding through inhibition of the PET process<sup>3</sup> and ability to bind several biologically relevant cations. Yet, very few studies have investigated the potential of crown ether appended iridium complexes.<sup>4,5</sup> We report herein the synthesis of two novel heteroleptic iridium complexes (1, 2) bearing two aza-15-crown-5 ethers. Complex 2 showed outstanding on-off luminescence triggered by the specific binding of Mg<sup>2+</sup>, which would represent an interesting chemosensor as magnesium is one of the most important biologically relevant metals. In addition, complex 2 has great potential as a molecular switch due to its very clear on and off states.

The aza-15-crown-5 ether phenylpyridines (az-ppy) used as cyclometalating ligands were synthesized with yields of 40–42% by Pd-catalyzed cross-coupling reactions of the corresponding bromophenylpyridine with aza-15-crown-5 ether (Scheme 1).<sup>6</sup> The cationic heteroleptic iridium(III) complexes (1, 2) were obtained by a two-step procedure<sup>7</sup> involving the synthesis of a cyclometalated dichloro-bridged diiridium dimer and its subsequent cleavage with a neutral 5,5'-dimethyl-2,2'-bipyridine. The previously reported complex  $3^8$  was used as a reference to discuss the effects of substitution.

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The absorption spectrum of **3** in CH<sub>3</sub>CN at 298 K shows a classical intense high energy absorption band between 220–320 nm assigned to intraligand (IL) ( $\pi$ – $\pi$ \* bpy and az-ppy) transitions, and weaker absorption shoulders above 320 nm assigned to metal-to-ligand charge-transfer (MLCT) ( $d\pi$ (Ir)– $\pi$ \*(bpy and az-ppy)) transitions. The absorption spectra of **1** and **2** are composed of similar IL and MLCT bands plus additional bands centered at 480 nm for **2** (Fig. 2) and from 320–450 nm for **1**. These bands are assigned to an overlap of the MLCT bands and intraligand charge transfer (ILCT) transitions originating from the azacrown nitrogen atoms as suggested by their disappearance upon protonation. These assignments are consistent with literature data<sup>2,9–11</sup> and in accordance with our TD-DFT calculations (Fig. 3).

The stability constants of 1 and 2 with a series of alkali and alkaline-earth metal ions ( $M = Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ) were determined by UV-visible titrations in acetonitrile with increasing amounts of metal ions. The titrations of 1 by the metal ions showed very small spectral variations, preventing the determination of the stability constants and suggesting low affinity. On the contrary, 2 showed a blue shift of the spectra and the disappearance of the ILCT band upon coordination of metal ions (Fig. 1), in agreement with their binding to the aza-crown ether moiety. These results underline the crucial impact of the substitution position of the binding group on its coordination properties.

TD-DFT calculations were performed on model complexes, in which the crown ether moiety was replaced by a dimethylamino group to simulate the free complexes (**M1**, **M2**, see ESI<sup>†</sup>) and by their protonated counterparts to simulate the metallated complexes (**M1-H**, **M2-H**, see ESI<sup>†</sup>) to simplify the calculations without altering the chromophoric part of the receptor. This approach has been adopted successfully in



Scheme 1 Synthesis of complex 2. (a) Aza-15-crown-5 ether, Pd(OAc)<sub>2</sub>, P(*t*-Bu)<sub>3</sub>, *t*-BuONa, toluene. (b) IrCl<sub>3</sub>·3H<sub>2</sub>O, 2-ethoxyethanol/H<sub>2</sub>O (3 : 1). (c) 5,5'-Dimethyl-2,2'-bipyridine, AgClO<sub>4</sub>, 1,2-dichloroethane/CHCl<sub>3</sub> (2 : 1).

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**Fig. 2** UV-visible titration of **2** with magnesium perchlorate. [**2**] =  $1.0 \times 10^{-5}$  M, CH<sub>3</sub>CN. Inset shows the fit (line) of the experimental data (dots) at 258 nm.



**Fig. 3** Experimental absorption spectra of **1** ([**1**] =  $1.00 \times 10^{-5}$  M, CH<sub>3</sub>CN) (line) and TD-DFT-simulated absorption spectra of its model **M1** (sticks). Isodensity plots of the 5 transitions with the biggest oscillator strength (isodensity value 0.03).

reported semi-empirical and TD-DFT calculations.<sup>12,13</sup> The calculated absorption transitions showed a good fit with the experimental spectra for both the free (**1** given as an example, Fig. 3) and metallated complexes, suggesting the pertinence of our model and the use of TD-DFT calculations to predict absorption properties of such complexes. Moreover the plot of the molecular orbitals corresponding to the five transitions with highest oscillator strength of **1** confirmed the attribution of the absorption bands above 320 nm to a mixing of ILCT (s8, s11, s12, s19) and MLCT (s13) transitions (Fig. 3 and ESI†).

Statistical processing of the spectrophotometric data for **2** supported the formation of 1:1 and 2:1 M:L species corresponding to the successive ligation of two metal ions to the two crown ether moieties of the az-ppy with values of log  $K_1 = 3.93(4)$  and log  $K_2 = 2.8(1)$  for Na<sup>+</sup>, log  $K_1 = 4.58(4)$ 

and log  $K_2 = 2.8(1)$  for Mg<sup>2+</sup>, log  $K_1 = 6.1(1)$  and log  $K_2 = 3.2(2)$  for Ca<sup>2+</sup>. It can be noted that the spectral variations upon coordination of K<sup>+</sup> (r = 1.38 Å) were negligible, suggesting very low binding affinity and reflecting the mismatch of size with the aza-15-crown-5 cavity (r = 0.85–1.1 Å).<sup>14</sup> The variation of the binding constants with the nature of the cation is in agreement with that reported for other systems bearing aza-15-crown-5 ether ionophores.<sup>15</sup> Considering that the two free crown-ether binding sites are equivalent and independent (as suggested by <sup>1</sup>H NMR) we can deduce a strong coordination of the first metal ion to **2** with negative cooperativity towards the second binding ( $4K_2/K_1 < 1$ ).<sup>16</sup>

The emission spectra in degassed acetonitrile showed a complete extinction of luminescence of 1 and 2 ( $\Phi = 0.00$ ,  $\lambda_{\rm ex}$  = 380 nm, Fig. 4) compared to the model complex 3  $(\Phi = 0.20, \lambda_{em} = 558 \text{ nm}, \lambda_{ex} = 400 \text{ nm})^8$  with no crown ether moiety. This quenching effect is due to classic PET from the nitrogen atom of the aza-crown ether to the iridium(III) center.<sup>3</sup> Complex 1 showed no significant increase of luminescence upon binding of cations as a result of its low binding ability. Cation binding by 2, bearing the aza-15-crown-5 ether groups in the *para*-position (relative to the iridium atom) of the az-ppy phenyl group, exhibited an outstanding on-switching of the luminescence in the blue-green region upon specific coordination of  $Mg^{2+}$  ( $\Phi = 0.15$ ,  $\lambda_{em} = 475$  and 507 nm,  $\lambda_{ex} = 380$  nm), whereas its Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> complexes remained non emissive (Fig. 4). The emission of cationic iridium(III) complexes containing diimine ligands commonly arises from a mixed excited-state containing <sup>3</sup>IL and <sup>3</sup>MLCT transitions, that is responsible for the multiple emission maxima (or shoulders) observed. Our results corroborated recent studies on iridium complexes bearing benzylsulfonyl-17 and perfluorophenyl-<sup>18</sup> phenylpyridine, which showed that the position of the substitution plays a decisive role in the emission wavelength tuning. In particular, the metallated aza-crown ethers act like withdrawing substituents (as opposed to their donating effect when they are metal-free), inducing a stabilisation of the HOMO of  $2-Mg^{2+}$  and a subsequent blue shift of 51 nm compared to 3 ( $\lambda_{em} = 558$  nm).

This cation-triggered luminescence can be rationalised by analogy with the kinetic models proposed by Schanze and MacQueen for the interpretation of cation coordination on the



**Fig. 4** Emission spectra of **2** and **2**-M<sup>*n*+</sup>. [**2**] =  $1.0 \times 10^{-5}$  M,  $[M^{n+}]/[2] = 2000$ .  $\lambda_{ex} = 380$  nm. Solvent: degassed CH<sub>3</sub>CN. Inset: Photograph of samples under ambient light (top) and UV irradiation (bottom,  $\lambda_{ex} = 365$  nm).



Scheme 2 Kinetic model of possible decay pathways of 2.

photophysics of a crown-ether-appended Re(1) complex<sup>19</sup> and by Tung and coworkers on a Pt(II)-crown ether complex.<sup>15</sup> The similar mechanism suggested for  $2-M^{n+}$  is described by Scheme 2 and suggests that, in addition to the normal radiative and nonradiative pathways  $(k_r, k_{nr})$ , the <sup>3</sup>MLCT excited state can also decay via a nonradiative path involving the dissociation of the crowned cation  $(k_{\text{off}})$  followed by the rapid internal conversion to a non-emitting low-lying <sup>3</sup>LLCT state  $(k_{\rm ic})$ <sup>20</sup> We suggest this dissociation pathway to be responsible for the non-emissive nature of the metal complexes of 1 and 2 with the exception of  $2 \cdot Mg^{2+}$ . The specific on-triggering of **2** by  $Mg^{2+}$  is due to its much higher charge density  $(Na^+: 0.05, K^+: 0.10, Ca^{2+}: 0.24, Mg^{2+}: 0.75)$ <sup>21</sup> inducing a stronger interaction between Mg<sup>2+</sup> and the aza-crown nitrogen leading to normal radiative and nonradiative decay of the <sup>3</sup>MLCT state ( $k_r$ ,  $k_{nr}$ ) rather than to cation dissociation  $(k_{on}, k_{off})$ . This strong binding of Mg<sup>2+</sup> by the aza-crown ether nitrogen is supported by the fact that the absorption spectrum of  $2-Mg^{2+}$  is almost identical to the protonated 2. It can be noted that the long emission lifetime of  $2-Mg^{2+}$  $(\tau = 2.45 \ \mu s \text{ in acetonitrile})$  together with its high sensitivity towards O<sub>2</sub> quenching is in accordance with an emission originating from phosphorescence resulting from the enhancement of the spin-orbit coupling.<sup>4</sup>

In conclusion we report a new phosphorescent aza-15crown-5-ether appended heteroleptic iridium complex (2) showing outstanding  $Mg^{2+}$  specificity and unambiguous on (2- $Mg^{2+}$ ) and off (free 2) states (Fig. 3, Inset) with a good quantum yield, suggesting promising future development in the fields of chemosensors or molecular switches. Moreover, to the best of our knowledge, this study is the first example of substitution effect on chelation-induced luminescence properties in iridium complexes. The drastic structure/properties differences between the two complexes considered in this work suggested metal binding as a new powerful and convenient color and intensity tuning strategy for iridium complexes. In order to draw a more complete picture of the potential of these molecules a systematic study of an extended series of complexes is under way.

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