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First examples of luminescent zinc(II)-bisquinoxalinato complexes: Synthesis, spectroscopic and theoretical studies

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ABSTRACT

Four novel homoleptic zinc(II) complexes were prepared in high yield from *para*-substituted 2,3-diphenyl-5-hydroxyquinoxaline ligands, $\mathbf{LH^n}$, giving $\mathbf{[Zn(L^n)_2]}$. Density functional theoretical calculations were performed to probe the influence of the variation in *para*-substitution on the ligands. The calculations suggest that ligand-centred character appears to dominate the HOMO and LUMOs. Experimental electrochemical and spectroscopic characterisation showed that the subtle variations in absorption and emission wavelengths are due to ligand-dominated transitions that are influenced by electronic nature of the *para*-substituted phenyl units in coordinated $\mathbf{L^n}$, in both solution and the solid states.

1. Introduction

In recent years there has been an increasing interest in metal complexes with luminescent properties for use in a multitude of areas, in particular photovoltaics, OLEDs, responsive probes and biological imaging [1]. These complexes contain chromophores, which can be modified in order to tune the wavelength of emitted light. 8-Hydroxyquinoline metal complexes are some of the most reliable electro-transporting and emitting materials used in OLEDs due to their thermal stability, high fluorescence and electron transporting mobility [2]. Whilst there have been numerous reports on metal ion complexes of Al(III) containing commercially available 8-hydroxyquinoline derivatives [1f,3], by comparison, relatively few describe the incorporation of substituted hydroxyquinoline ligands into zinc(II) complexes. OLEDs based upon the benchmark tris(8-hydroxyquinolinato)aluminium, Alq_3, (Fig. 1) complex possess an electroluminescence efficiency (quantum yield) which is limited to a maximum of 25% [4]. However, the zinc(II) analogue, Znq_2, (Fig. 1) has better injection efficiency, lower operating voltage, and higher quantum yield [5]. Therefore, zinc complexes of this type have a great potential in electroluminescent (EL) devices. Recently, it has been reported that the emission wavelength of these complexes can be easily tuned by modifying the 8-hydroxyquinoline ligands in the 2-, 5- and 7-positions [6]. Here we report the first examples of zinc(II) complexes bearing substituted hydroxyquinoxaline ligands in which the 2- and 3-positions contain *para*-substituted phenyl groups. The synthesis, characterisation and spectroscopic properties are reported herein.

2. Experimental

2.1. Materials and Instruments

All reactions were performed with the use of vacuum line and Schlenk techniques. Reagents were commercial grade and were used without further purification. ^{1}H NMR spectra and were run on an NMR-FT Bruker 400 MHz spectrometer and were recorded in d^6-DMSO. ^{1}H NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. Mass spectra were carried out by the staff at Cardiff University. High resolution mass spectra were carried out by at the EPSRC National Mass Spectrometry Service at Swansea University. UV–Vis studies were performed on a Jasco V-570 spectrophotometer as DMF solutions (5×10^{-5} M). Photophysical data were obtained on a JobinYvon–Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module as MeOH solutions or in the solid state. Emission spectra were uncorrected and excitation spectra were instrument corrected. The pulsed source was a Nano-LED configured for 372 nm output operating at 500 or 100 kHz. Luminescence lifetime profiles were obtained using the JobinYvon–Horiba FluoroHub single photon counting module and the data fits yielded the lifetime values using the provided DAS6 deconvolution software. The ligands $\mathbf{LH^n}$ (n = 1–4) were prepared as previously reported [7].

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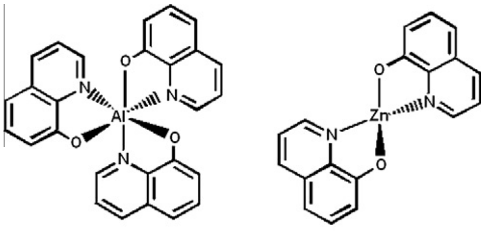

[Alq$_3$] [Znq$_2$]

Fig. 1. The structures of Alq$_3$ and Znq$_2$.

2.2. Electrochemistry

Electrochemical studies were carried out using a Parstat 2273 potentiostat in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire and the working electrode a platinum (1.0 mm diameter) disc. The reference was a silver wire separated from the test solution by a fine-porosity frit. Solutions (10 ml DMF) were 1×10^{-3} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in $[NBu_4][PF_6]$ as the supporting electrolyte. Solutions were de-oxygenated with a stream of N_2 gas and were maintained under a positive pressure of N_2 during all measurements. Potentials are quoted versus the $[Fe(\eta^5\text{-}C_5H_5)_2]^+/[Fe(\eta^5\text{-}C_5H_5)_2]$ couple ($E^{0\prime}$ = + 0.45 V in DMF) [8] as the internal standard.

2.3. DFT studies

All calculations were performed on the Gaussian 03 program [9]. Geometry optimisations were carried out without constraints using the B3PW91 functional. The LANL2DZ basis set was used for the Zn centres, and was invoked with pseudo-potentials for the core electrons, a 6–31G(d,p) basis set for all coordinating atoms with a 6–31G basis set for all remaining atoms. All optimisations were followed by frequency calculations to ascertain the nature of the stationary point (minimum or saddle point).

2.4. Synthesis

2.4.1. ***[Zn(L^1)$_2$]***

$Zn(OAc)_2 \cdot 2H_2O$ (25 mg, 0.11 mmol), **LH^1** (69 mg, 0.23 mmol), Na_2CO_3 (122 mg, 1.15 mmol) and 2-methoxyethanol (8 ml) were heated at 110 °C for 14 h. The mixture was cooled to room temp and the product precipitated by the slow addition of water (25 ml). The orange powder was filtered, washed with water and dried *in vacuo*. Yield 66 mg, 0.10 mmol (88%). ^{1}H NMR (400 MHz, d^6-DMSO) δ_H = 7.71 (2H, app. t {coincident dd}, $^3J_{HH}$ = 8.1 Hz), 7.36–7.28 (14H, m), 7.15 (2H, d, $^3J_{HH}$ = 8.3 Hz), 6.99 (2H, d, $^3J_{HH}$ = 7.5 Hz), 6.87 (6H, m) ppm. EI MS found *m/z* 660.1, calculated *m/z* 660.1 for [M]$^+$. HR MS found *m/z* 658.1344, calculated *m/z* 658.1342 for $[C_{40}H_{26}O_2N_4Zn_1]^+$. UV–Vis (DMF): λ_{max} (ε dm^3 mol^{-1} cm^{-1}) = 302(44 500), 320(38 150), 465(2400) nm.

2.4.2. ***[Zn(L^2)$_2$]***

Prepared similarly from $Zn(OAc)_2 \cdot 2H_2O$ (16 mg, 0.07 mmol) and **LH^2** (69 mg, 0.15 mmol). Yield 64 mg, 0.67 mmol (91%). ^{1}H NMR (400 MHz, d^6-DMSO) δ_H = 7.72 (2H, app. t, $^3J_{HH}$ = 8.2 Hz), 7.63 (2H, d, $^3J_{HH}$ = 8.3 Hz), 7.51 (4H, d, $^3J_{HH}$ = 8.4 Hz), 7.19 (4H, d, $^3J_{HH}$ = 8.5 Hz), 7.13 (2H, d, $^3J_{HH}$ = 8.4 Hz), 7.09–6.92 (8H, m) ppm. Negative ion MS found *m/z* 1010.7, calculated *m/z* 1011.1 for [M+Cl]$^-$. HR MS found *m/z* 1004.7473, calculated *m/z* 1004.7462 for $[C_{40}H_{22}O_2N_4Br_4Cl_1Zn_1]^-$. UV–Vis (DMF): λ_{max} (ε dm^3 mol^{-1} cm^{-1}) = 300(54 500), 320(57 300), 363(16 350), 459(2650) nm.

2.4.3. ***[Zn(L^3)$_2$]***

Prepared similarly from $Zn(OAc)_2 \cdot 2H_2O$ (32 mg, 0.14 mmol) and **LH^3** (95 mg, 0.29 mmol). Yield 86 mg, 0.24 mmol (82%). ^{1}H NMR (400 MHz, d^6-DMSO) δ_H = 7.66 (2H, app. t, $^3J_{HH}$ = 8.3 Hz), 7.22 (2H, d, $^3J_{HH}$ = 8.4 Hz), 7.11 (6H, app. t, $^3J_{HH}$ = 8.2 Hz), 6.97 (4H, d, $^3J_{HH}$ = 7.9 Hz), 6.91 (4H, br s), 6.45 (4H, d, $^3J_{HH}$ = 7.8 Hz) ppm. ES MS found *m/z* 717.2, calculated *m/z* 717.2 for [M+H]$^+$. HR MS found *m/z* 715.2055, calculated *m/z* 715.2046 for $[C_{44}H_{35}O_2N_4Zn_1]^+$. UV–Vis (DMF): λ_{max} (ε dm^3 mol^{-1} cm^{-1}) = 294(16 600), 353(3500), 475(400) nm.

2.4.4. ***[Zn(L^4)$_2$]***

Prepared similarly from $Zn(OAc)_2 \cdot 2H_2O$ (17 mg, 0.08 mmol) and **LH^4** (57 mg, 0.16 mmol). Yield 53 mg, 0.07 mmol (88%). ^{1}H NMR (400 MHz, d^6-DMSO) δ_H = 7.63 (2H, app. t, $^3J_{HH}$ = 8.5 Hz), 7.14 (4H, d, $^3J_{HH}$ = 8.6 Hz), 7.06 (2H, d, $^3J_{HH}$ = 8.1 Hz), 6.94 (6H, m), 6.82 (4H, d, $^3J_{HH}$ = 8.6 Hz), 6.25 (4H, d, $^3J_{HH}$ = 8.5 Hz), 3.74 (6H, s), 3.46 (6H, s) ppm. ES MS found *m/z* 803.2, 819.2 and 844.1, calculated *m/z* 803.2, 819.3 and 844.2 for [M+Na]$^+$, [M+K]$^+$ and [M+MeCN+Na]$^+$ respectively. HR MS found *m/z* 801.1656, calculated *m/z* 801.1662 for $[C_{44}H_{34}O_6N_4Na_1Zn_1]^+$. UV–Vis (DMF): λ_{max} (ε dm^3 mol^{-1} cm^{-1}) = 301(11 800), 329(8400), 377(5000), 479(550) nm.

3. Results and discussion

3.1. Synthesis and characterisation

Four *para*-substituted 2,3-diphenyl-5-hydroxyquinoxaline ligands, **LH$^{1-4}$** (1 = *p*-H, 2 = *p*-Br, 3 = *p*-Me, 4 = *p*-OMe) were prepared in a two-step reaction (Scheme 1) as previously reported [7]. Firstly, 2-amino-3-nitrophenol was reduced by heating to reflux in acidic EtOH for 14 h in the presence of zinc dust, giving the corresponding 2,3-diamino compound. Subsequent condensation with a range of substituted diones in refluxing EtOH for 16 h gave the desired ligands as yellow powders.

The neutrally charged homoleptic complexes **[Zn(L^n)$_2$]** (*n* = 1–4) were isolated, following addition of base to a reaction mixture composition of 2:1 ligand to $Zn(OAc)_2 \cdot 2H_2O$ in 2-methoxyethanol, in excellent yields of 82–91%. The complexes were isolated by addition of water to the reaction mixture as bright orange/red powders. They were characterised in the solution state using ^{1}H NMR, UV–Vis. and luminescence spectroscopy and cyclic voltammetry. EI mass spectrometry revealed the parent ions [M]$^+$ for **[Zn(L^1)$_2$]**, negative ion revealed [M+Cl]$^-$ for **[Zn(L^2)$_2$]** and ES mass spectrometry revealed the protonated parent ions [M+H]$^+$ for **[Zn(L^3)$_2$]** and **[Zn(L^4)$_2$]**.

3.2. Density functional theory (DFT) studies

In order to understand the nature of the electronic transitions within this class of complex, DFT calculations (computed using the B3PW91 hybrid orbital) were undertaken. In these examples, an assessment of the frontier orbitals provided a qualitative insight into the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels.

Firstly, for the quinoxalinato complexes described here the lowest energy configurations show that the predicted structures have one of the two phenyl rings twisted out of the plane for both ligands in each case. The calculated energy levels of both the HOMO and HOMO-1 are sufficiently similar (ΔE < 0.2 eV) to be considered isoenergetic in all cases. The same is true of the LUMO and LUMO+1. Both the HOMO and LUMO are located primarily on the quinoxalinato ligand with little or no orbital coverage on the metal centre. The HOMO lies exclusively on one of the quinoxalinato ligands with the HOMO-1 (a mirror image) on the second