DALTON
FULL PAPER

Synthesis and photophysical characterisation of luminescent zinc complexes with 5-substituted-8-hydroxyquinolines

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New 5-substituted-8-hydroxyquinoline ligands HL_n (**1**–**3**), in which the quinoline and the *p-N,N*-dimethylphenyl fragments are connected through the –N=N– (**1**), –CH=N– (**2**) or $–CH_2–NH–$ (**3**) group, were designed and synthesised. Their reaction with a Zn(II) salt gave the pertinent $Zn(L_n)_2$ complexes (**4**–**6**). The compounds **1**–**4** and **6** are stable in solution and their photophysical properties were explored. Zinc complexes **4** and **6** are both luminescent (**4**, λ_{em}: 620 nm, $\Phi < 1 \times 10^{-4}$; **6**, λ_{em}: 475 nm, $\Phi = 7 \times 10^{-3}$), although the states responsible for the radiative deactivation processes were different: CT in nature for **4** and from a π–π* transition localised on the quinoline fragment for **6**. The roles exerted by both the metal and bridge on the photophysical properties are discussed.

Introduction

Organic Light Emitting Devices (OLEDs) are based on materials which feature easily tuneable photophysical properties and good processability. To this end, although several complexes of different polycyclic aromatic ligands with Be,[1] Mg,[1a] Zn,[1a,b,d,2] Ga,[3] Ir,[4] Pt,[5] Eu[1a,d,6] or Tb[1a] are currently being tested, the most popular OLED electroluminescent material is the aluminium co-ordination compound containing the 8-hydroxyquinoline (HQ) ligand, AlQ_3.[7]

The HQ chelating ligand is an aromatic molecule whose electronic and geometric features can be modulated through appropriate substituents. It is indeed known that the electronic π–π* transitions in AlQ_3 are centred on the ligands and that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are localized on the phenoxide and on the pyridyl rings, respectively.[1a,b] Thus, it has been predicted and proved that while an electron-donating substituent in the 5 position of the quinoline causes a red-shift in the absorption spectrum of the corresponding complexes, an electron-withdrawing substituent needs to be in positions 2 or 4 in order to cause the same effect.[1a,2a,5a,8,9] These results account for different HOMO–LUMO gaps, and the electron transport properties of these complexes can be properly regulated by changing the electronic effects that the substituents exert on the quinolinate skeleton.

In this area we have focused our attention on a series of 5-substituted-8-hydroxyquinoline ligands (hereafter HQ′–AB–$C_6H_4NMe_2$, Fig. 1) in which different AB bridges (*i.e.* **1**: –N=N–; **2**: –CH=N–; **3**: $–CH_2–NH–$) were used to connect the metal chelating entity to the $C_6H_4NMe_2$ group. The rationale behind the approach above is justified by the influence the addition of substituents to the quinoline skeleton exerts on the emission colour of the material and by the expectation that bulky groups surrounding the metal co-ordination sphere would prevent both aggregation and crystallization, thus yielding molecules suitable for the formation of homogeneous amorphous films which are essential for good device performance.[10]

The present paper reports the synthesis and photophysical characterisation of new HQ′–AB–$C_6H_4NMe_2$ species and their zinc complexes.

Results and discussion

Synthesis

Ligand **1** was synthesized following the procedure described in the literature for homologous compounds,[11] while **2** was obtained through reaction of 5-formyl-8-hydroxyquinoline[12] with *N,N*-dimethyl-1,4-phenylenediamine and **3** was prepared by catalytic hydrogenation of **2**. Finally, the respective zinc complexes **4**–**6** were obtained by treating the ligands **1**–**3** with zinc chloride.

The ligands and their complexes were characterised by IR and ^1H NMR spectroscopy[13] and their purity confirmed by elemental analysis. Together, these data confirmed the chemical structure of the expected products (**1**–**3** in Fig. 1 and **4**–**6** in Fig. 2).

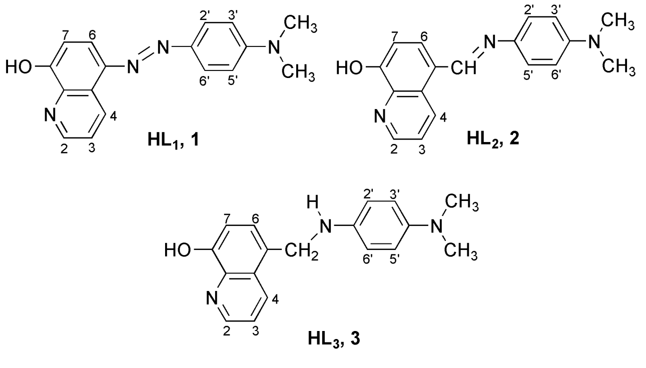

Fig. 1 Chemical structures and proton numbering scheme for the HL_n ligands **1**–**3**.

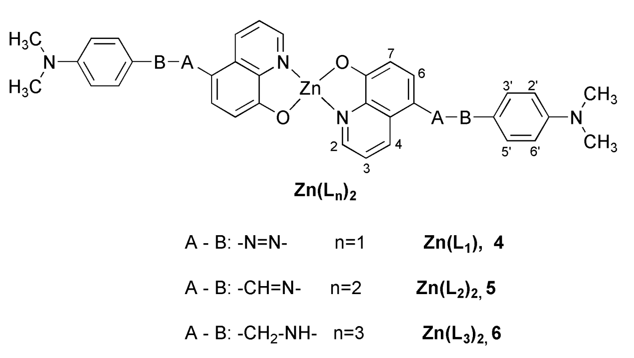

Fig. 2 Chemical structures and proton numbering scheme for the $Zn(L_n)_2$ complexes **4**–**6**.

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Table 1 Photophysical spectral data for **1** and **3** and absorption and emission spectral data for **2**, **4** and **6**

	Absorption		Emission	
Compound	Solvent	λ_{abs}/nm (ε/M^{-1} cm^{-1})	λ_{em}/nm	Φ
1	CH_2Cl_2	235(23600), 261(15800), 323(4700), 442(25500), 460(sh)	n.o.	—
4	DMSO	430 (sh), 490 (55600)	620	$<10^{-4}$
2	CH_2Cl_2	237(33500), 263(15300), 312 (18200), 407 (16100)	570	$<10^{-4}$
3	CH_2Cl_2	328 (2700)	n.o.	—
6	DMSO	338 (41000), 408 (28500)	475	0.007

The synthesised compounds are solid and stable in solution, except for **5**, whose imino group hydrolyses yielding the bis-[(5-formyl)-8-hydroxyquinolinate]Zn complex.[13]

Spectroscopic properties

The photophysical properties of the **1**–**4** and **6** species (Table 1) were investigated in solution and the fluorescence quantum yields were measured with the method described by Demas and Crosby[14] using $[Ru(bipy)_3]Cl_2$ (bipy = 2,2′-bipyridine; $\Phi = 0.028$ in aerated water[15]) as standard.

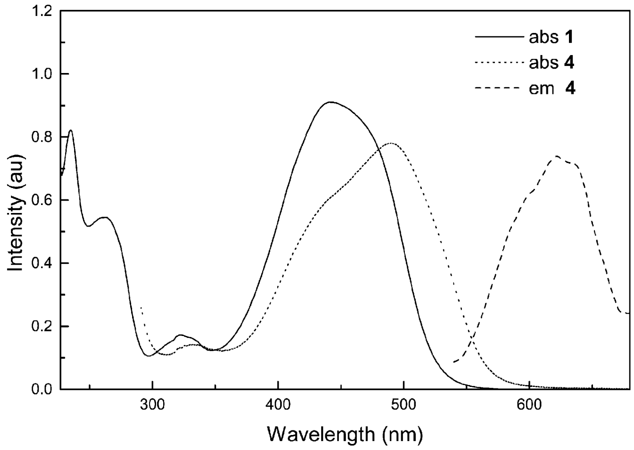

Fig. 3 Absorption spectrum of **1** and absorption and emission spectra of **4**.

The ground-state absorption spectrum of **1** (Fig. 3) shows transitions attributable to the quinoline (235, 261 and 323 nm) and to the azobenzene (442 nm) chromophores and could safely be assigned taking into account the literature data.[16,17] It is known that the HQ absorption spectrum shows three bands, the first one in the range of 220–250 nm (Φ–Φ* process), the second at about 270 nm (σ_N–π_{py}* transition from the electron pair of the nitrogen atom which is part of the pyridine ring to the LUMO) and the third in the range of 300–320 nm (HOMO–LUMO transition, corresponding to the $\pi_{ph} \longrightarrow \pi_{py}^*$ excitation). Moreover, azobenzenes show three accessible excited states to which three absorption bands, in the visible and near UV spectral region, are related. In particular, the lowest energy absorption at approximately 430–440 nm, arises from the partially forbidden n–π* process; the band at about 310 nm (for the more stable at the photostationary equilibrium *trans* –N=N– form) is due to the allowed π–π* transition and the highest energy band which appears in the 230–240 nm region involves the –N=N– bonded benzene rings. However, in the present cases both the bands expected around 310 nm and in the 230–240 nm range are superimposed on absorptions of the HQ′– fragment. In addition, it should be pointed out that the shoulder observed at 460 nm in the absorption spectrum for **1**, which was absent in the spectra of azobenzenes without substituents in the *para*-positions, could be assigned to a charge transfer (CT) from the lone pair of the nitrogen atom of the $-NMe_2$ group to empty orbitals of the quinoline aromatic rings.

1 does not emit while **4** shows a band at 620 nm (Fig. 3). Since the emission involves the CT energy, the observed behaviour could tentatively be explained assuming that the energy of the CT state of **1** is higher than that of the $n_N\pi^*$ related state (Fig. 4). In such circumstances, whilst **1** undergoes a thermal deactivation, **4** radiatively deactivates as the CT state becomes the lowest excited one by effect of the lowering of the LUMO energy which takes place upon zinc co-ordination. This model seems to be supported by the well defined low energy band, probably CT in nature, detected at 490 nm in the absorption spectrum of **4** (Fig. 3).

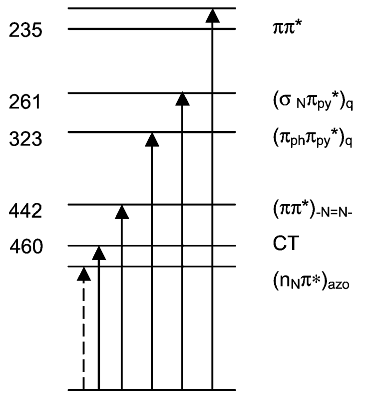

Fig. 4 States diagram for **1**; wavelengths (in nm, left) and transitions (right).

Only the spectrum of ligand **2** was recorded because of the instability of the zinc complex **5** towards hydrolysis. The electronic spectrum of **2** (Fig. 5) shows three bands (at 237, 263 and 312 nm) attributable to transitions, slightly perturbed by the imino substituent, localised on the quinolinate rings. A low energy band, at 407 nm, can be assigned to a CT transition from the $-NMe_2$ group to the quinoline rings mediated by the –CH=N– π electrons. In the absorption spectrum of the amino

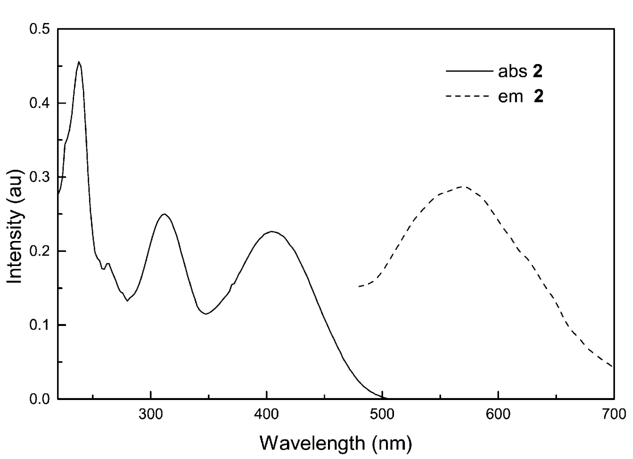

Fig. 5 Absorption and emission spectra of **2**.

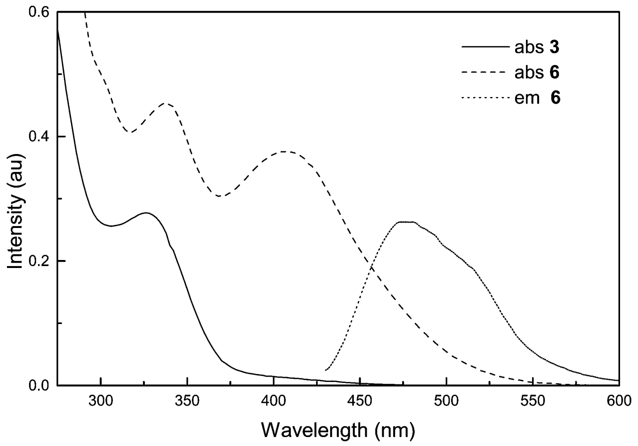

Fig. 6 Absorption spectrum of **3** and absorption and emission spectra of **6**.

ligand **3**, wherein the –C=N– bond is replaced by the saturated –CH_2–NH– linkage (Fig. 6), this band disappears. The above mentioned CT state is the lowest excited one, at which takes place the fluorescence of **2** (Fig. 5).

In the examined range, while the absorption spectrum of **3** shows only a broad band at 328 nm, corresponding to a π_{ph}–π_{py}* transition of the quinolinate chromophore, the spectrum of **6** shows two pronounced absorption bands, attributable to quinoline localised transitions at 338 nm (σ_N–π_{py}*) and 408 nm (π_{ph}–π_{py}*). Therefore it can be concluded that the metal complexation preserves the identity of the electronic states. Ligand **3** does not emit whereas **6** shows, in DMSO solution, a fluorescence emission at 475 nm, with an absolute quantum yield of 0.7%.

Conclusion

The photophysical properties of some 5-substituted-8-hydroxyquinolines have been investigated. The comparison of their absorption spectra has confirmed that the bands, positioned in the 300–330 nm range, are sensitive to the electronic effect exerted by the different substituents. Interestingly, from these data it can be inferred that, with respect to the unsubstituted HQ ligand, both the –N=N–$C_6H_4NMe_2$ and –CH_2–NH–$C_6H_4NMe_2$ groups displayed an electron donating ability (–CH_2–NH–$C_6H_4NMe_2$ > –N=N–$C_6H_4NMe_2$) whereas the –CH=N–$C_6H_4NMe_2$ molecular fragment exhibited an electron withdrawing effect. Moreover, the emission properties appeared to be strongly perturbed by these substituents. This effect can be attributed to the nature of the AB bridge since the nπ* state carried by the –N=N– linkage suppresses fluorescence in **1** and the –CH=N– group makes **2** luminescent through a radiative deactivation which originates from a charge transfer from the NMe_2 electron lone pair to the quinolinate fragment. This CT process requires the –CH=N– double bond, so that, as observed for **3**, the replacement of the –CH=N– with the –CH_2–NH– bridge causes the loss of luminescence.

The preparation of new zinc complexes with different 5-substituted-8-hydroxyquinolines was successful. The known electroluminescent ZnQ_2 complex,[1a,18] in dichloromethane solution displayed absorptions at 341 and 377 nm and emission at 540 nm. With reference to ZnQ_2, some spectral modification, induced by the two substituents for which the test was possible (*i.e.* –N=N–$C_6H_4NMe_2$ and –CH_2–NH–$C_6H_4NMe_2$) were noteworthy. Thus, while in **4** a new CT state involving the quinolinate core was responsible for low energy bands in the absorption spectrum and luminescent properties, in **6** the substituent did not modify the identity of the ZnQ_2 electronic states. Its absorption spectrum showed a red-shift of the band at lower energy, as expected for an electron donating substituent in the 5 position, and the Stokes' shift, lower than that for ZnQ_2, accounts for a small change in molecular structure when passing from the ground to the excited state.

In solution, **4** and **6** emit at 620 nm (orange) and 475 nm (greenish blue) respectively, so this outcome illustrates the tunability of the emission energy in species whose molecular structures feature the same peripheral group and different AB bridges. Since it can be envisaged that these compounds experience similar intermolecular interactions, the result of this preliminary research can be used for the preparation of stable mixed homogeneous films of broad band luminescent molecular materials.

Experimental

General procedures

The infrared spectra in KBr were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped for reflectance measurements. The ^{1}H NMR spectra were recorded on a Bruker WH-300 spectrometer in $CDCl_3$ or DMSO solutions, with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer CHNS/O. The thermal behavior was monitored with a Zeiss Axioscope polarizing microscope equipped with a Linkam CO 600 heating stage. Absorption spectra were recorded with a Perkin-Elmer Lambda 900 spectrophotometer. Corrected luminescence spectra were obtained with a Perkin-Elmer LS-50B spectrofluorimeter. Selection of excitation and emission wavelengths were performed with monochromators or optical filters.

All the commercially available chemicals were used without further purification.

Preparation of ligands, 1–3

HL_1, 5-[(4′-*N*,*N*-Dimethyl)phenylazo]-8-hydroxyquinoline (1). 1.72 mL of 12 M hydrochloric acid (0.75 g, 20.0 mmol) was slowly added to a stirred solution of 0.94 g (6.89 mmol) of *N*,*N*-dimethyl-1,4-phenylenediamine dissolved in the minimum amount of H_2O (10 mL). The resulting solution was cooled in an ice bath and an aqueous sodium nitrite (0.51 g, 7.44 mmol) solution (5 mL) was added dropwise. The diazonium chloride so-formed was then coupled with 8-hydroxyquinoline (1.0 g, 6.89 mmol) dissolved in 7.92 mL of aqueous sodium hydroxide 2 N solution (0.63 g, 20.0 mmol) and the reaction mixture was stirred for 1 h at 0 °C, and then allowed to reach room temperature slowly. The resulting suspension was acidified with dilute hydrochloric acid and the precipitate which formed was collected by filtration, dissolved in $CHCl_3$ and the resulting solution dried over anhydrous Na_2SO_4. The crude red product, obtained after removal of the solvent under reduced pressure, was purified by recrystallisation from $CHCl_3$–EtOH (1.14 g, 53%). Mp 214–216 °C. Anal. calc. for $C_{17}H_{16}N_4O$: C, 69.84; H, 5.52; N, 19.16%. Found: C, 69.40; H, 5.41; N, 19.38%. $\tilde{\nu}_{max}$/cm^{-1} 3317 (stretching OH), 2900 (stretching aliphatic CH), 1600, 1575, 1566, 1519, 1502, 1444 (stretching N=N), 1278, 1250, 1210, 1151 (KBr). δ_H ($CDCl_3$) 9.30 (1H, d, *J* 8.82 Hz, H^4), 8.86 (1H, d, *J* 4.41 Hz, H^2), 7.96 (3H, m, H^6 and $H^{2',6'}$), 7.58 (1H, dd, *J* 4.41 and 8.82 Hz, H^3), 7.26 (1H, d, *J* 8.10 Hz, H^7), 6.80 (2H, d, *J* 8.82 Hz, $H^{3',5'}$), 3.11 (6H, s, $N(CH_3)_2$).

HL_2, 5-[(4′-*N*,*N*-Dimethyl)phenyliminomethyl]-8-hydroxyquinoline (2). 0.79 g (5.77 mmol) of *N*,*N*-dimethyl-1,4-phenylenediamine in 5 mL of EtOH was added to a suspension of 5-formyl-8-hydroxyquinoline (1.0 g, 5.77 mmol) in EtOH, (10 mL). The resulting mixture was stirred at reflux for 4 h and then slowly cooled to room temperature. The crude green product, collected by filtration, was purified by recrystallisation from $CHCl_3$–*n*-hexane (1.24 g, 74%). Mp 173–175 °C. Anal. calc. for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42%. Found: C, 73.97; H, 5.72; N, 14.61%. $\tilde{\nu}_{max}$/cm^{-1} 2850 (stretching aliphatic CH), 1609, 1504, 1476, 1190 (KBr). δ_H ($CDCl_3$) 9.93 (1H, dd, *J* 1.83 and 8.55 Hz, H^4), 8.83 (1H, s, CH=N), 8.82 (1H, m, H^2), 7.85 (1H, d, *J* 8.55 Hz, H^6), 7.58 (1H, dd, *J* 4.26 and 8.55 Hz, H^3), 7.30 (2H, d, *J* 9.15 Hz, $H^{2',6'}$), 7.22 (1H, d, *J* 8.40 Hz, H^7), 6.80 (2H, d, *J* 9.15 Hz, $H^{3',5'}$), 3.00 (6H, s, $N(CH_3)_2$).

HL_3, 5-[(4′-*N*,*N*-Dimethyl)phenylaminomethyl]-8-hydroxyquinoline (3). A catalytic amount of Pd/C and then 0.04 g (1.03 mmol) of $NaBH_4$ were added to 0.50 g (1.72 mmol) of **2** in EtOH (10 mL) The resulting mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the crude product was dissolved in $CHCl_3$ and then filtered on Celite. The crude yellow product, obtained after removal of the solvent under reduced pressure, was purified by recrystallisation from $CHCl_3$–*n*-hexane (0.19 g, 64%). Mp 190–193 °C. Anal. calc. for $C_{18}H_{19}N_3O$: C, 73.70; H, 6.53; N, 14.32%. Found: C, 73.70; H, 6.00; N, 14.10%. $\tilde{\nu}_{max}$/cm^{-1} 3363 (stretching N–H), 2838 (stretching aliphatic CH), 1505, 1476, 1214, 1194 (KBr). δ_H ($CDCl_3$) 8.78 (1H, d, *J* 4.02 Hz, H^2), 8.44 (1H, d, *J* 8.52 Hz, H^4), 7.48–7.42 (2H, m, H^3 and H^6), 7.10 (1H, d, *J* 7.62 Hz, H^7), 6.77–6.69 (4H, m, $H^{2',6'}$ and $H^{3',5'}$), 4.55 (2H, s, NCH_2), 2.84 (6H, s, $N(CH_3)_2$).

Preparation of complexes, 4–6

$Zn(L_1)_2$, Bis{5-[(4′-*N*,*N*-dimethyl)phenylazo]-8-hydroxyquinolinate}zinc(II) (4). A hot solution of **1** (0.30 g, 1.03 mmol) in acetic acid (20 mL) was added dropwise to a stirred solution containing zinc chloride (0.07 g, 0.51 mmol) and ammonium acetate (1.15 g, 14.90 mmol), dissolved in 30 mL of H_2O. After 5 h of vigorous stirring at reflux, the resulting red solid was filtered off, washed with water, suspended in hot chloroform, filtered and then dried *in vacuo* (0.32 g, 95%). Mp 290–292 °C (dec.). Anal. calc. for $C_{34}H_{30}N_8O_2Zn{\cdot}2H_2O$: C, 59.70; H, 5.01; N, 16.38%. Found: C, 59.56; H, 4.82; N, 16.29%. $\tilde{\nu}_{max}$/cm^{-1} 2894 (stretching aliphatic CH), 1462 (stretching N=N), 1387, 1362, 1257, 1227, 1198 (KBr). δ_H (DMSO) 9.77 (2H, br s, H^2), 9.13 (2H, br s, H^4), 8.40 (2H, br s, H^6), 8.16 (6H, m, H^3 and $H^{2',6'}$), 7.20 (6H, m, H^7 and $H^{3',5'}$), 3.73 (12H, s, $N(CH_3)_2$).

$Zn(L_2)_2$, Bis{5-[(4′-*N*,*N*-dimethyl)phenyliminomethyl]-8-hydroxyquinolinate}zinc(II) (5). The same procedure for obtaining **4** was used to synthesise **5** using CH_3OH as solvent. The compound was obtained as a red solid (0.21 g, 59%). Mp 238–241 °C (dec.). Anal. calc. for $C_{36}H_{32}N_6O_2Zn$: C, 66.93; H, 4.99; N, 13.01%. Found: C, 66.50; H, 4.84; N, 13.12%. $\tilde{\nu}_{max}$/cm^{-1} 2885 (stretching aliphatic CH), 1600, 1561, 1502, 1465, 1336 (KBr). δ_H (DMSO) 10.12 (2H, br s, H^4), 8.82 (2H, s, CH=N), 8.75 (2H, m, H^2), 7.95 (2H, d, *J* 7.83 Hz, H^6), 7.76 (2H, m, H^3), 7.25 (4H, d, *J* 7.80 Hz, $H^{2',6'}$), 6.85 (2H, m, H^7), 6.77 (4H, d, *J* 7.80 Hz, $H^{3',5'}$), 2.85 (12H, s, $N(CH_3)_2$).

$Zn(L_3)_2$, Bis{5-[(4′-*N*,*N*-dimethyl)phenylaminomethyl]-8-hydroxyquinolinate}zinc(II) (6). The same procedure for obtaining **4** was used to synthesise **6** using a mixture H_2O–CH_3OH (v/v 1/1) as solvent. The compound was obtained as a green solid (0.24 g, 70%). Mp 320–323 °C (dec.). Anal. calc. for $C_{36}H_{36}N_6O_2Zn{\cdot}2H_2O$: C, 63.02; H, 5.88; N, 12.25%. Found: C, 63.65; H, 5.45; N, 12.13%. $\tilde{\nu}_{max}$/cm^{-1} 3346 (stretching N–H), 2837 (stretching aliphatic CH), 1597, 1573, 1505, 1463, 1326 (KBr). As **6** was insoluble in common solvents, no NMR data are available.

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