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Fine-tuning the luminescent properties of metal-chelating 8-hydroxyquinolines through amido substituents in 5-position

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Abstract

New series of 5-substituted-8-hydroxyquinolines HL_n (**1–6**) bearing aliphatic or aromatic amido groups were synthesised. The chelating ability of these ligands toward the zinc(II) ion was tested and the photophysical characterisation of the resulting complexes $(ZnL_n)_2 \cdot 2H_2O$ (**7–12**) is reported and compared to those of the uncomplexed ligands. The photophysical data of **1–6** revealed interesting differences between aliphatic (**1–3**) and aromatic (**4–6**) amido-substituted species which, however, are no longer evident upon metal complexation. In fact while the ligands **1–3** showed a very high quantum yield (**2**, $\lambda_{em} = 470$ nm; $\Phi = 0.22$) higher than that of the unsubstituted HQ compound, the ligands **4–6** displayed low quantum yield, similar to that of the complexes **7–12**, which was in turn lower than that of $ZnQ_2 \cdot 2H_2O$. The behaviour of these compounds is discussed with particular reference to the possibility of controlling the photophysical properties of such compounds through selective modification of the amido substituents.

Keywords: Zinc complexes; 5-Amido-substituted-8-hydroxyquinoline ligands; Luminescence

1. Introduction

Photoluminescence is an intrinsic molecular property of great interest for the preparation of advanced materials required for applications such as organic light emitting devices (OLED) [1] or liquid crystals displays (LCD) [2]. The requisites of a luminescent substance for practical industrial purposes are good processability and the possibility of fine-tuning the photophysical features in order to adapt material performance to the desired application. Thus, with regard to the molecular materials which are based on coordination compounds, the role of the metal-bonded ligands is of paramount importance for achieving such aims.

8-Hydroxyquinoline (HQ) is a chelating ligand with emitting properties which has been extensively exploited in the synthesis of luminescent metal complexes [3], and to improve the opto-electronic output of this class of materials, studies involving either HQ or HQ-like species are currently under way [4].

In this context, the role of a series of substituents placed on position 5 of the HQ rings was considered focusing, in particular, on the nature of different bridges (i.e., —N=N—, —CH=N—, —CH_2—NH—) for connecting the 8-hydroxyquinoline core to the $C_6H_4NMe_2$ group [5].

Since the emission maxima of all the considered compounds resulted, in varying extent, to be red-shifted with reference to that of HQ, obtained data suggested a useful way to modulate the luminescence properties of these species: 5-amido-substituted quinolines may be ideal for studying photophysical modulations of useful compounds.

Here we report the synthesis of a series of different aliphatic and aromatic 5-amido-substituted-8-hydroxyquinolines (Fig. 1) and their photoluminescent properties. The chelating ability of these ligands toward the zinc(II) ion was tested and the photophysical characteristics of the resulting complexes are also reported and compared to those of the uncomplexed ligands.

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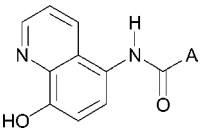


Fig. 1. General structure of the 5-amido-substituted-8-hydroxyquinolinate ligands.

2. Experimental

2.1. 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 behaviour was monitored with a Zeiss Axioscope polarising 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, equipped with a Hamamatsu R-928 photomultiplier tube. Photoluminescent quantum yields were measured with the method described by Demas and Crosby [6] using $[Ru(bipy)_3]Cl_2$ (bipy = 2,2′-bipyridine); $\Phi = 0.028$ in aerated water [7] as standard. Luminescence lifetimes were obtained with IBH single-photon counting apparatus whose operating lamp employed nitrogen or deuterium. Selection of excitation and emission wavelengths was performed with monochromators or optical filters. The experimental uncertainty in the band maximum for absorption and luminescence spectra is 2 nm; that for luminescence intensity is 20%. The time resolution of the single-photon spectrometer is 200 ps, the uncertainty of the evaluated lifetimes is 8% and that of the extinction coefficient is 10%. All emissions are confirmed by excitation spectra.

All the commercially available chemicals were used without further purification.

2.2. Preparation of ligands, **1**–**6**

2.2.1. HL_1, 5-acetylamino-8-hydroxyquinoline hydrochloride (**1**)

Acetyl chloride (0.096 ml, 0.105 g, 1.341 mmol) was added dropwise to 5-amino-8-hydroxyquinoline dihydrochloride (0.250 g, 1.072 mmol) in pyridine *dry* at 0 °C. The solution was stirred for 6 h at 0 °C. Thereafter the solvent was removed under reduced pressure, the residue dissolved in methanol and the insoluble white solid filtered off. Ethyl acetate was added to the solution; the green solid, which formed, was collected by filtration, washed with ethyl acetate, chloroform and dried in vacuo. Yield 61%. Mp 240–243 °C$_{dec}$ *Anal*. Calc. for $C_{11}H_{10}N_2O_2 \cdot HCl$: C, 55.36; H, 4.64; N, 11.74. Found: C, 55.08; H, 4.63; N, 11.48%. IR (KBr, cm^{-1}): *v* 3227 (stretching N—H), 2914 (stretching CH_3), 1689 (stretching C=O), 1598, 1530 (bending N—H), 1381, 1304. ^{1}H NMR (CD_3OD, ppm): δ 9.14 (d, 1H, *J* 8.67 Hz, H^4), 9.08 (d, 1H, *J* 4.32 Hz, H^2), 8.10 (dd, 1H, *J* 8.67 and 4.32 Hz, H^3), 7.77 (d, 1H, *J* 8.67 Hz, H^6), 7.46 (d, 1H, *J* 8.67 Hz, H^7), 2.30 (s, 3H, CH_3).

The homologous compounds **2**–**6** were prepared similarly.

2.2.2. HL_2, 5-dodecinoylamino-8-hydroxyquinoline hydrochloride (**2**)

The green crude product was recrystallised from methanol; the green solid which formed was collected by filtration, washed with ethyl acetate, chloroform and dried in vacuo. Yield 45%. Mp 193–195 °C. *Anal*. Calc. for $C_{21}H_{30}N_2O_2 \cdot HCl$: C, 66.56; H, 8.24; N, 7.39. Found: C, 66.49; H, 8.11; N, 7.13%. IR (KBr, cm^{-1}): *v* 3242 (stretching N—H), 2914 (stretching aliphatic CH), 1677 (stretching C=O), 1596, 1557 (bending N—H), 1519, 1470, 1391, 1307. ^{1}H NMR (DMSO-d$_6$, ppm): δ 10.26 (s, 1H, N—H), 9.04 (d, 1H, *J* 0.96 Hz, H^2), 9.00 (d, 1H, *J* 8.79 Hz, H^4), 8.07–8.03 (m, 1H, H^3), 7.72 (d, 1H, *J* 8.35 Hz, H^6), 7.50 (d, 1H, *J* 8.31 Hz, H^7), 2.48 (t, 2H, *J* 7.80 Hz, O=C—CH_2), 1.70–0.85 (m, 21H, aliphatic protons).

2.2.3. HL_3, 5-(1′-adamantanoyl)amino-8-hydroxyquinoline hydrochloride (**3**)

Yellow solid. Yield 36%. Mp > 300 °C. *Anal*. Calc. for $C_{20}H_{22}N_2O_2 \cdot HCl$: C, 66.94; H, 6.46; N, 7.81. Found: C, 66.80; H, 6.66; N, 7.62%. IR (KBr, cm^{-1}): *v* 3280 (stretching N—H), 2909 (stretching aliphatic CH), 1649 (stretching C=O), 1598, 1552 (bending N—H), 1504, 1386, 1361, 1301. ^{1}H NMR (CD_3OD, ppm): δ 9.07 (d, 1H, *J* 4.03 Hz, H^2); 8.88 (dd, 1H, *J* 8.72 and 1.34 Hz, H^4), 8.09 (dd, 1H, *J* 8.72 and 5.37 Hz, H^3), 7.64 (d, 1H, *J* 8.05 Hz, H^6), 7.46 (d, 1H, *J* 8.71 Hz, H^7), 2.12 (m, 9H, aliphatic protons), 1.86 (m, 6H, aliphatic protons).

2.2.4. HL_3', 5-(1′-adamantanoyl)amino-8-hydroxyquinoline (**3′**)

White solid obtained by heating **3** at 160 °C under vacuum for 5 days. Mp > 300 °C. *Anal*. Calc. for $C_{20}H_{22}N_2O_2$: C, 73.34; H, 6.81; N, 8.65. Found: C, 73.29; H, 6.86; N, 8.73%. IR (KBr, cm^{-1}): *v* 3300 (stretching N—H), 2905 (stretching aliphatic CH), 1640 (stretching C=O), 1598, 1583 (bending N—H), 1508, 1397, 1372, 1280 (KBr). ^{1}H NMR (CD_3OD) 8.83 (d, 1H, *J* 2.01 Hz, H^2); 8.15 (d, 1H, *J* 7.38 Hz, H^4), 7.55 (dd, 1H, *J* 8.72 and 4.03 Hz, H^3), 7.30 (d, 1H, *J* 8.71 Hz, H^6), 7.11 (d, 1H, *J* 8.05 Hz, H^7), 2.12 (m, 9H, aliphatic protons), 1.86 (m, 6H, aliphatic protons).

*2.2.5. HL_4, 5-benzoylamino-8-hydroxyquinoline hydrochloride (**4**)*

Green solid. Yield 64%. Mp 253–256 °C. *Anal*. Calc. for $C_{16}H_{12}N_2O_2 \cdot HCl$: C, 63.90; H, 4.36; N, 9.31. Found: C, 63.78; H, 4.19; N, 9.13%. IR (KBr, cm^{-1}): *v* 3250 (stretching N—H), 1662 (stretching C=O), 1596, 1557 (bending N—H), 1515, 1389, 1359, 1306, 1250. ^1H NMR (CD_3OD, ppm): δ 9.07–9.10 (m, 2H, H^2 and H^4); 8.05–8.10 (m, 3H, H^3 and $H^{2',6'}$), 7.82 (d, 1H, *J* 8.31 Hz, H^6), 7.55–7.68 (m, 3H, $H^{3',5'}$ and $H^{4'}$), 7.50 (d, 1H, *J* 8.31 Hz, H^7).

*2.2.6. HL_5, 5-(4′-tert-butyl)-benzoylamino-8-hydroxyquinoline hydrochloride (**5**)*

Green solid. Yield 63%. Mp 241–243 °C *Anal*. Calc. for $C_{20}H_{20}N_2O_2 \cdot HCl$: C, 67.32; H, 5.93; N, 7.85%. Found: C, 67.19; H, 5.99; N, 8.06%. IR (KBr, cm^{-1}): *v* 3210 (stretching N—H), 2961 (stretching aliphatic CH), 1631 (stretching C=O), 1599, 1553 (bending N—H), 1525, 1386, 1365, 1248. ^1H NMR (CD_3OD, ppm): δ 9.04 (d, 1H, *J* 4.47 Hz, H^2); 8.94 (d, 1H, *J* 8.61 Hz, H^4), 8.02 (d, 2H, *J* 8.61 Hz, $H^{2',6'}$), 7.96–8.00 (m, 1H, H^3), 7.76 (d, 1H, *J* 8.25 Hz, H^6), 7.62 (d, 2H, *J* 8.61 Hz, $H^{3',5'}$), 7.44 (d, 1H, *J* 8.25 Hz, H^7), 1.39 (s, 9H, $C(CH_3)_3$).

*2.2.7. HL_6, 5-(1′-naphthoyl)-amino-8-hydroxyquinoline hydrochloride (**6**)*

Green solid. Yield 59%. Mp 272–275 °C. *Anal*. Calc. for $C_{20}H_{14}N_2O_2 \cdot HCl$: C, 68.48; H, 4.31; N, 7.98. Found: C, 68.10; H, 4.19; N, 8.10%. IR (KBr, cm^{-1}): *v* 3227 (stretching N—H), 1661 (stretching C=O), 1598, 1558 (bending N—H), 1513, 1385, 1302, 1250. ^1H NMR (CD_3OD, ppm): δ 9.18 (d, 1H, *J* 8.76 Hz, H^4); 9.09 (d, 1H, *J* 4.77 Hz, H^2), 8.35–8.39 (m, 1H, $H^{8'}$), 8.03–8.12 (m, 3H, H^3, $H^{2'}$ and $H^{4' \text{ or } 5'}$), 7.96–8.01 (m, 2H, H^6 and $H^{5' \text{ or } 4'}$), 7.58–7.67 (m, 3H, $H^{3'}$, $H^{6'}$ and $H^{7'}$), 7.53 (d, 1H, *J* 8.04 Hz, H^7).

*2.3. Preparation of complexes, 7–**12***

*2.3.1. $Zn(L_1)_2$, bis[5-acetylamino-8-hydroxyquinolinate] zinc(II) dihydrate (**7**)*

A hot solution of **1** (0.1 g, 0.419 mmol) in methanol (10 ml) was added dropwise to a stirred solution containing zinc chloride (0.029 g, 0.209 mmol) and ammonium acetate (0.468 g, 6.075 mmol), dissolved in 30 ml of H_2O. After 5 h of vigorous stirring at reflux, the resulting green solid was filtered off, washed with water and methanol, filtered and then dried in vacuo. Yield 69%. Mp > 300 °C. *Anal*. Calc. for $C_{22}H_{18}N_4O_4Zn \cdot 2H_2O$: C, 52.45; H, 4.40; N, 11.12. Found: C, 52.71; H, 4.27; N, 10.96%. IR (KBr, cm^{-1}): *v* 2920–2860 (stretching CH_3), 1654 (stretching C=O), 1576 (bending N—H), 1553, 1504, 1469, 1388, 1296. ^1H NMR (DMSO-d_6, ppm): δ 9.55 (s, 2H, N—H), 8.59 (br s, 2H, H^2), 8.28 (d, 2H, *J* 7.98 Hz, H^4), 7.51–7.47 (m, 2H, H^3), 7.23 (br s, 2H, H^6), 6.84 (br s, 2H, H^7).

The homologous compounds **8**–**12** were prepared similarly.

*2.3.2. $Zn(L_2)_2$, bis-[5-dodecinoylamino-8-hydroxyquinolinate] zinc(II) dihydrate (**8**)*

Green solid. Yield 84%. Mp > 300 °C_{dec}. *Anal*. Calc. for $C_{42}H_{58}N_4O_4Zn \cdot 2H_2O$: C, 64.31; H, 7.97; N, 7.14. Found: C, 64.58; H, 7.88; N, 7.26%. IR (KBr, cm^{-1}): *v* 2920 (stretching aliphatic CH), 1653 (stretching C=O), 1576 (bending N—H), 1542, 1504, 1468, 1387, 1389. ^1H NMR data are not available because of the scarce solubility.

*2.3.3. $Zn(L_3)_2$, bis-[5-(1′-adamantanoyl)-8-hydroxyquinolinate] zinc(II) dihydrate (**9**)*

Green solid. Yield 70%. Mp > 300 °C. *Anal*. Calc. for $C_{40}H_{42}N_4O_4Zn \cdot 2H_2O$: C, 64.56; H, 6.23; N, 7.53. Found: C, 64.25; H, 6.19; N, 7.42%. IR (KBr, cm^{-1}): *v* 2904 (stretching aliphatic CH), 1640 (stretching C=O), 1578 (bending N—H), 1492, 1465, 1388. ^1H NMR (DMSO-d_6, ppm): δ 9.06 (s, 2H, N—H); 8.67 (br s, 2H, H^2), 8.10 (d, 2H, *J* 8.07 Hz, H^4), 7.56 (m, 2H, H^3), 7.13 (br s, 2H, H^6), 6.81 (br s, 2H, H^7), 2.04–2.00 (m, 30H, aliphatic protons).

*2.3.4. $Zn(L_4)_2$, bis-[5-benzoylamino-8-hydroxyquinolinate] zinc(II) dihydrate (**10**)*

Green solid. Yield 88%. Mp > 300 °C. *Anal*. Calc. for $C_{32}H_{22}N_4O_4Zn \cdot 2H_2O$: C, 61.21; H, 4.17; N, 8.92. Found: C, 60.95; H, 4.21; N, 8.68%. IR (KBr, cm^{-1}): *v* 1647 (stretching C=O), 1579 (bending N—H), 1507, 1487, 1387, 1094 (KBr). ^1H NMR (DMSO-d_6, ppm): δ 10.13 (s, 2H, N—H); 8.76 (br s, 2H, H^2), 8.31 (d, 2H, *J* 8.22 Hz, H^4), 8.07 (d, 4H, *J* 7.14 Hz, $H^{2',6'}$), 7.52–7.64 (m, 8H, H^3, $H^{4'}$ and $H^{3',5'}$), 7.37 (d, 2H, *J* 8.10 Hz, H^6), 6.85 (d, 2H, *J* 8.10 Hz, H^7).

*2.3.5. $Zn(L_5)_2$, bis-[5-(4′-tert-butyl)benzoylamino-8-hydroxyquinolinate] zinc(II) dihydrate (**11**)*

The green crude product was purified by recrystallisation from pyridine/water. Yield 80%. Mp > 300 °C. *Anal*. Calc. for $C_{40}H_{38}N_4O_4Zn \cdot 2H_2O$: C, 64.91; H, 5.72; N, 7.57. Found: C, 65.15; H, 5.53; N, 7.61%. IR (KBr, cm^{-1}): *v* 2963 (stretching aliphatic CH), 1647 (stretching C=O), 1576 (bending N—H), 1491, 1465, 1387. ^1H NMR (DMSO-d_6, ppm): δ 10.07 (s, 2H, N—H); 8.76 (br s, 2 H, H^2), 8.29 (d, 2H, *J* 8.25 Hz, H^4), 8.00 (d, 4H, *J* 8.25 Hz, $H^{2',6'}$), 7.61 (m, 2H, H^3), 7.56 (d, 4H, *J* 8.25 Hz, $H^{3',5'}$), 7.34 (d, 2H, *J* 7.71, Hz, H^6), 6.84 (d, 2H, *J* 7.71 Hz, H^7), 1.34 (s, 18H, $C(CH_3)_3$).

*2.3.6. $Zn(L_6)_2$, bis-[5-(1′-naphthoyl)amino-8-hydroxyquinolinate] zinc(II) dihydrate (**12**)*

Green solid. Yield 76%. Mp > 300 °C. *Anal*. Calc. for $C_{40}H_{26}N_4O_4Zn \cdot 2H_2O$: C, 65.99; H, 4.15; N, 7.70. Found: C, 65.94; H, 4.13; N, 7.77%. IR (KBr, cm^{-1}): *v*

1650 (stretching C=O), 1578 (bending N—H), 1493, 1470, 1407. ^{1}H NMR (DMSO-d_6, ppm): δ 10.55 (s, 2H, N—H); 9.06 (br s, 2H, H^2), 8.78 (d, J 7.80 Hz, 2H, H^4), 8.61–8.64 (m, 2H, $H^{8'}$), 8.24–8.39 (m, 6H, $H^{2'}$, $H^{4'}$ and $H^{5'}$), 7.46–7.95 (m, 10H, H^3, H^6, $H^{3'}$, $H^{6'}$ and $H^{7'}$), 7.21 (br s, 2H, H^7).

3. Results and discussion

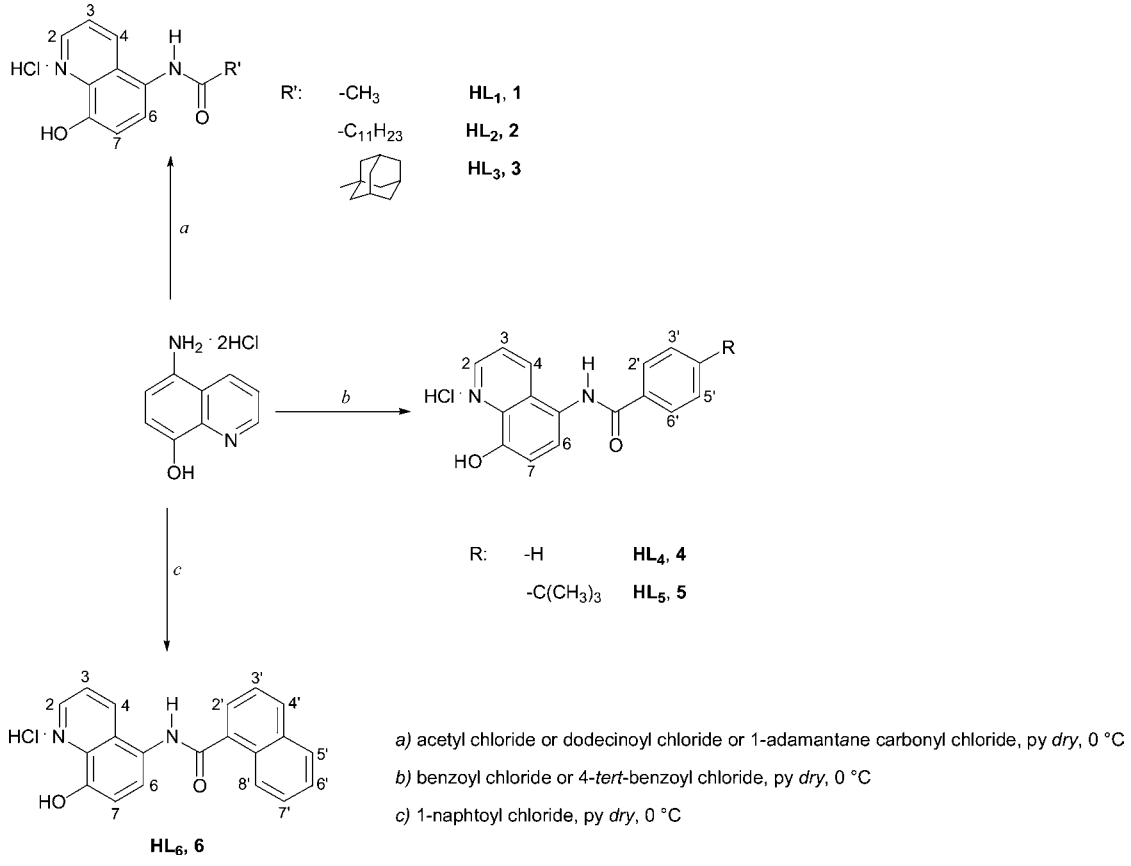
3.1. Synthesis

The preparation of ligands (**1**–**6** in Scheme 1) was accomplished by adapting the syntheses reported in the literature [8]. The reactions between 5-amino-8-hydroxyquinoline dihydrochloride and each of the selected acyl chlorides gave the desired hydrochloride ligands, $HL_n \cdot HCl$, which were yellow–green solids, with yields ranging from 36% to 64%. Several attempts devoted to prepare species without hydrochloric acid were performed, but the only compound obtained without hydrochloric acid was the ligand containing the adamantane derivative, HL'_3 (**3′**), through the heating of the parent $HL_3 \cdot HCl$ (**3**) species under vacuum (Section 2).

The characterisation of the reaction products **1**–**6** ($HL_n \cdot HCl$ in Scheme 1) was performed by elemental analyses, which confirmed the reported stoichiometry, IR and ^{1}H NMR spectroscopy. In particular, the formation of the —NHCO— amido linkage is apparent from the IR spectra (Section 2) which showed the N—H stretching frequency (in the 3280–3210 cm^{-1} region, diagnostic of secondary amides) and the C=O absorption band (at about 1689–1631 cm^{-1}).

Two molecules of **1**–**6**, treated with $ZnCl_2$, formed the corresponding dihydrate $Zn(L_{1-6})_2 \cdot 2H_2O$ complexes (**7**–**12** in Fig. 2) in good yields (69–88%). These compounds are green solids which were characterised by IR and ^{1}H NMR spectroscopy and their purity confirmed by elemental analyses.

Compared with those of the respective ligands, the IR spectra of the zinc complexes showed a shift of the C=O stretching frequencies, and the appearance of two strong bands in the 1510–1460 cm^{-1} region which was attributable to the coordination of the quinoline fragment to the metallic centre. Elemental analyses of all the species **7**–**12** confirmed the general formula $Zn(L_{1-6})_2 \cdot 2H_2O$. Along with the X-ray crystallographic data reported in the literature concerning the structure of the parent



Scheme 1. Synthesis of HL_{1-6} ligands **1**–**6**.

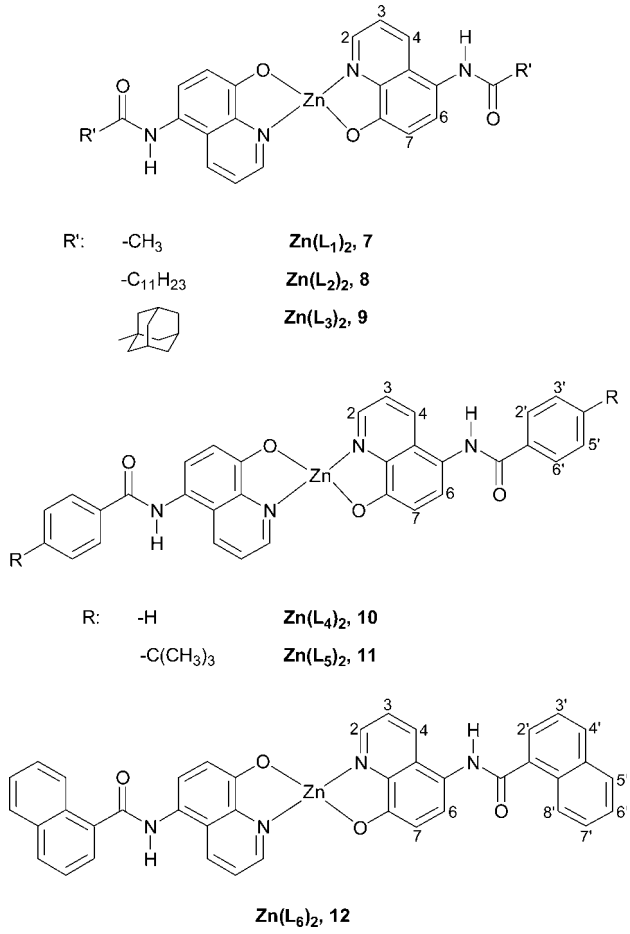


Fig. 2. Chemical structures and proton numbering scheme for the $Zn(L_{1-6})_2$ complexes **7**–**12**.

$ZnQ_2 \cdot 2H_2O$ complex [9], it is possible to suggest that in **7**–**12** the zinc also adopts an octahedral coordination geometry with two mutually *trans* quinoline fragments in the equatorial positions and two water molecules in the axial positions.

3.2. Spectroscopic properties

The photophysical properties of the novel species were investigated in DMSO at room temperature (Table 1).

As the ligand containing the adamantane amido substituent was available in two forms, **3** and **3′**, the absorption spectra of these species (Fig. 3) will be compared and discussed first. Both compounds exhibited an absorption maximum at 332 nm; moreover, **3** showed a shoulder at 390 nm which disappeared in very dilute solutions; on the contrary, upon the addition of hydrochloric acid, this feature increased in intensity while the band at 332 nm decreased. These outcomes indicate the presence of an equilibrium between two species absorbing at 332 and at 390 nm, respectively.

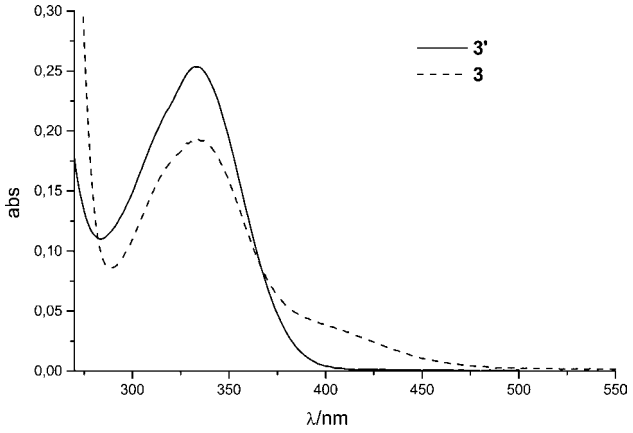


Fig. 3. Absorption spectra of compounds **3** and **3′** in DMSO solution (1.35×10^{-4} M).

Table 1
Photophysical properties of the synthesised compounds **1**–**12** in DMSO solution

Compound	Absorption[a]	Emission			
	λ (nm) (ε (M^{-1} cm^{-1}))	λ (nm)	Φ	Δ (cm^{-1})	τ (ns)
HQ	316 (3190)	416	0.005	7607	1.4[b]
1	334 (1780)	467	0.14	8526	14
2	334 (1760)	470	0.22	8310	15
3	332 (1870)	468	0.14	8753	12
4	333 (3055)	450	2.0 E-3	7807	<1
5	334 (4000)	452	2.0 E-3	7638	<1
6	340 (3600)	440	6.0 E-3	6684	<1
$ZnQ_2 \cdot 2H_2O$	340 (3112), 400 (3700)	534	0.04	6273	
7	344 (4100), 414 (5170)	598	0.9 E-3	7432	<1
8	344 (4200), 415 (5300)	592	1.8 E-3	7204	<1
9	344 (4600), 413 (5460)	597	0.8 E-3	7462	<1
10	344 (6500), 417 (6900)	584	1.0 E-3	6914	<1
11	344 (6570), 418 (6800)	584	3.0 E-3	6741	<1
12	344 (6200), 418 (6200)	602	1.5 E-3	7312	<1

[a] The ε values for **1**–**6** were calculated for a molecular weight corresponding to HL_n.
[b] In DMF; see [10].

Such results were further confirmed upon the addition of hydrochloric acid to **3′**, since the absorption maximum at 390 nm appeared and progressively increased with acid concentration while the 332 nm peak correspondingly decreased (Fig. 4). Such observations indicate that when **3** is dissolved in DMSO, an equilibrium between the protonated ($\lambda_{max} = 390$ nm) and the neutral form ($\lambda_{max} = 332$ nm) takes place. At the low solution concentration required for spectroscopic measurements, this equilibrium was almost completely shifted toward the neutral form. Worthy of note, HQ in DMSO displayed similar behaviour since, with the addition of concentrated HCl, the band centred at 316 nm (HQ form) decreased while the band at 364 nm (H_2Q^+ form [10]) increased.

As the absorption spectra of all the ligands **1**–**6** in dilute DMSO solution showed comparable features with **3′** it is possible to assume that the entire series of hydrochloride compounds are in equilibrium between the cationic and the neutral forms and that the recorded spectra can actually be assigned, for all the ligands under examination, to the HL_n species.

The ground-state absorption spectra of **1**–**6** (Table 1) show substantial uniformity with a sharp band at about 335 nm (Fig. 5) which was almost insensitive to solvent variation. According to the literature data [4c,11], this feature can be assigned to the π–π^* transition from a filled orbital localised on the quinoline phenoxide ring towards an antibonding molecular orbital localised on the pyridyl ring. This excitation, observed at 316 nm for HQ, is red-shifted, as expected from the electron-donating effect [12] exerted by the —NHCO— linkage, and appears to be unaffected by the nature of the A group (Fig. 1).

Regarding the luminescence properties, while HQ emits, protonated form H_2Q^+ does not [10,13]; likewise, in spite of the previously invoked equilibria, it is plausible that the emissions observed in DMSO (with maxima ranging from 440, **6**, to 470 nm, **2**) can be ascribed to the HL_n species only.

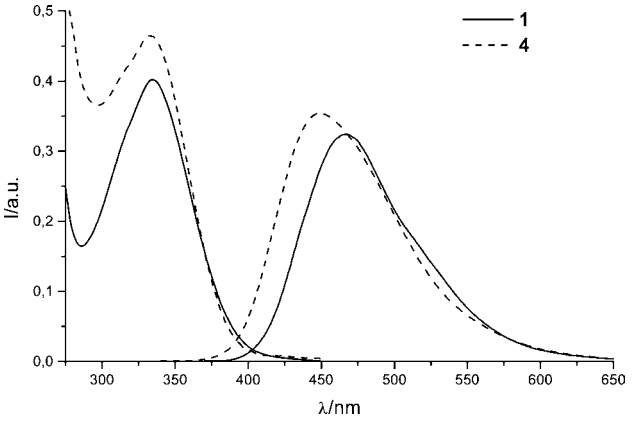


Fig. 5. Absorption and fluorescence spectra of **1** and **4** in DMSO solution.

The investigation of substituent effects on the photophysical properties of the ligands highlights a different behaviour between aliphatic and aromatic amido-substituted compounds. The emission maximum of the ligands (**1**–**3**) bearing aliphatic substituents was red-shifted with respect to those with aromatic substituents (**4**–**6**) (Table 1); moreover, the values of the photoluminescent quantum yield (Φ), the Franck–Condon shift (energy difference between absorption and emission maximum; Δ) and of the lifetime of the emitting state (τ) for **1**–**3** were considerably greater than those measured for **4**–**6**.

In the whole series of zinc complexes **7**–**12** no differences could be attributed to the nature of group A, as revealed by the absorption or emission spectra (Table 1) with all complexes showing two absorption maxima at 344 and ~415 nm, and an emission band peaking within the 590–600 nm range (Fig. 6 for **7** and **10**).

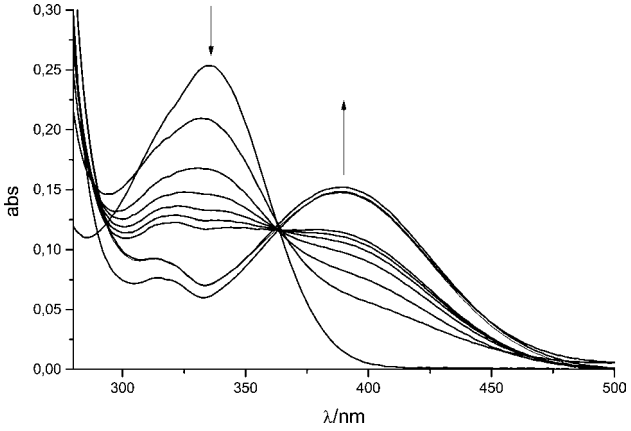


Fig. 4. Spectral changes induced by the addition of HCl to **3′** in DMSO solution.

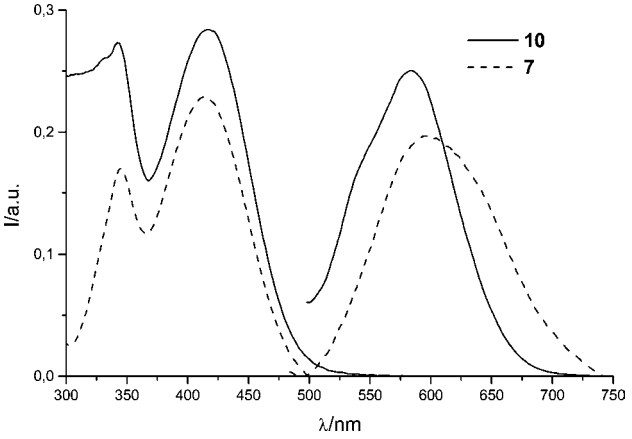


Fig. 6. Absorption and fluorescence spectra of **7** and **10** in DMSO solution.

The absorption bands are due to ligand-localised transitions slightly perturbed by the metal, as described previously for the $ZnQ_2 \cdot 2H_2O$ complex [4c,4d,4j,4k,4m] ($\lambda_{abs} = 340, 400$ nm; $\lambda_{em} = 534$ nm; Table 1); with respect to this reference compound, the lowest energy transition of **7**–**12** (which is responsible for the observed fluorescence) exhibited a bathochromic shift due to the electron-donating effect of the amido substituents [5]. The emission quantum yield of **7**–**12** was about 10^{-3} (i.e., one order of magnitude lower than that of $ZnQ_2 \cdot 2H_2O$), irrespective of the nature of the amido group.

4. Conclusion

A new series of 5-amido-substituted-8-hydroxyquinolines were synthesised by reaction of 5-amino-8-hydroxyquinoline with aliphatic or aromatic acylchlorides. These ligands preserved the metal chelating ability of the unsubstituted 8-hydroxyquinoline, allowing for the preparation of the corresponding zinc(II) derivatives.

Both the ligands (**1**–**6**) and the complexes (**7**–**12**) are stable compounds exhibiting interesting emission properties. The photophysical data obtained for **1**–**6** revealed differences between aliphatic (**1**–**3**) and aromatic amido-substituted species (**4**–**6**) which disappeared upon metal complexation. Indeed while the ligands **1**–**3** showed very high quantum yields which were higher than those of the unsubstituted HQ compound [14], the ligands **4**–**6** displayed very low quantum yields similar to those of all their complexes, which were in turn lower than that of $ZnQ_2 \cdot 2H_2O$ (Table 1). In addition, comparing the absorption and emission spectra of such compounds, the following differences were observed:

1. with respect to HQ, the main emission bands of **1**–**3** showed a more consistent red-shift than for **4**–**6**;
2. the values of Φ and τ of the excited state of **1**–**3** were in the range 0.14–0.22 and 12–15 ns, respectively, while for **4**–**6** these values ranged from 0.003 to 0.006 and less than 1 ns, respectively;
3. all the complexes **7**–**12** (irrespective of the different nature of the substituents) showed absorption and emission features which were only slightly influenced by solvent polarity, with the values of Φ and τ of the excited state being nearly 10^{-3} and 1 ns, respectively.

It is well established that the lack of fluorescence in HQ-related compounds is due to the occurrence of excited-state proton transfer (ESPT) which, involving the OH phenoxide group and the pyridyl nitrogen atom, transforms the neutral enolic form into its ketotautomer, which mainly de-excitates non-radiatively [13]. The interesting behaviour observed in the present cases might therefore be explained taking into account the occurrence of extended electronic delocalisation which is created by the addition of the amido substituent to HQ. Such an addition may either (i) alter the properties of the state associated with the observed absorption and emission bands or (ii) introduce some n–π^* character from a keto C=O-localised transition [15]. In fact, while the aromatic ring of compounds **4**–**6** could easily delocalise electron density on the $\pi^*_{C=O}$ orbital, thus increasing its energy, in compounds **1**–**3** which contain an aliphatic substituent such delocalisation could be more difficult. Consequently, with respect to compounds **4**–**6** an inversion of states could take place in **1**–**3**, and the high quantum yield emission, originating from the lowest excited state, would in this case have a partial n–π^* character. Instead, in **4**–**6** the emitting state is similar to that of the HQ system [13] and because of the ESPT, fluorescence is partially quenched.

In the zinc complexes, the n–π^* related state probably remains at higher energy, irrespective of the nature of the substituent, and fluorescence may thus originate from a π–π^* transition which is localised on the quinoline rings; in this case, the low quantum yield observed with respect to $ZnQ_2 \cdot 2H_2O$ could be attributed to an increased energy loss throughout the vibrating manifold in the excited state [16] as evidenced by the greater Δ values exhibited by these complexes with respect to the reference compound.

In conclusion, the spectroscopic studies carried out on the newly synthesised HQ derivatives clearly demonstrate that fine control of the photophysical properties is possible through the modification of substituents in position 5 of the 8-hydroxyquinoline rings. In particular, although the bridge connecting the HQ core to an aromatic group was found to be crucial for luminescence [5], we found that the aliphatic 5-amido substituents further enhanced photoluminescence, overcoming both the HQ and the $ZnQ_2 \cdot 2H_2O$ quantum yield.

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