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# Luminescent complexes of the zinc triad with *N*-substituted 8-amino-quinoline ligands: Synthesis and comparative study on the stability constants and related photophysical properties

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ABSTRACT

The potentially fluorescent terdentate ligand bis-quinolin-8-yl-amine (BQAH) yields the bis-chelate complexes $[M(BQAH)_2](ClO_4)_2$ (M = Zn, Cd, Hg) and the mono-chelate $[M(BQAH)Cl_2]$ (M = Zn, Cd). The aminic proton of the coordinated BQAH displays a remarkable acidity. Thus, in polar solvents ($CH_3CN$ and methanol) the formation of the deprotonated derivatives $[M(BQA)_2]$ and [M(BQA)Cl] is observed whose absorption and fluorescent spectra are identical with those of independently synthesized complexes (M = Zn). The affinity of the ligand BQAH with the metals of the zinc triad was studied in $CH_3CN$; the stability constants related to the complex $[M(BQAH)(CH_3CN)]^{2+}$ ($\beta_1$) and $[M(BQAH)_2]^{2+}$ ($\beta_2$) were determined and compared with those calculated in the case of the ligand 8-[(2-pyridylmethyl)amino]-quinoline (NNN(Qui)) in the same solvent. Owing to the enhanced rigidity of the ligand BQAH, a marked selectivity in coordinating the $Zn^{2+}$ cation with respect to the larger $Cd^{2+}$ was apparent. In the case of mercury, the equilibrium constant value was also confirmed by means of $^1H$ NMR technique. The low lying excited state of the BQAH and NNN(Qui) systems is ligand centered and fluo-solvato-chromism analysis reveals that in protic solvents an inter-molecular hydrogen bond between the aminic proton in the excited state and the solvent itself efficiently quenches the fluorescent signal. Coordination with metals induces a hypsochromic displacement of the absorbance maxima measured in $CH_2Cl_2$ with respect to those of the free ligands. On the contrary in $CH_3OH$ the complete deprotonation of the coordinated BQAH induces a bathochromic displacement of the absorption maxima at 480 nm. In $CH_3OH$ the fluorescent emissions of the mono- and bis-chelate deprotonated $BQA^-$ complexes at ≈600 nm display a very low quantum yield and a reduced Stokes shift as compared with that of the protonated species. Such an increase can be related to the enhanced rigidity of the deprotonated ligand inducing a tight coplanarity of the aromatic rings in the first excited state. Eventually the metal coordination, while reducing the energy of the fluorescent emission of both ligands in $CH_2Cl_2$, does not inhibit the non radiative relaxation pathways in the BQAH system.


## 1. Introduction

The use of chelating ligands bearing quinoline nitrogen as a coordinating atom represents an important target when coordination of Group Twelve metals is taken into consideration, since it combines two complementary and important features. As a matter of fact, the marked coordinating capability of the nitrogen coupled with the chromophoric characteristics of the quinoline ring [1] induces the formation of stable metal complexes with potential photophysical properties. Therefore, the monitoring of metals of the zinc triad, which heavily interfere with living organisms as bioactive species [2] and pollutants, by means of versatile spectrophotometric techniques represents an easily available and low cost analytical approach, as suggested by the impressive number of articles appeared so far [3].

Recently, we have published a paper dealing with the synthesis of some amine and thioether pyridine and quinoline derivatives in which their coordinative and photophysical properties when coordinated to zinc, cadmium and mercury were analyzed in detail [4]. We have now extended our investigation to the ligand di-quinolin-8-yl-amine (BQAH) with the aim of increasing the fluorescence intensity of the ensuing metal complexes. We have therefore determined the formation constants of the complexes by means of UV–Vis and $^1H$ NMR spectrometry. We have also determined the fluorescent characteristics of the ligands and of the derived complexes.

The ligand and the metal complexes studied are reported in Scheme 1.

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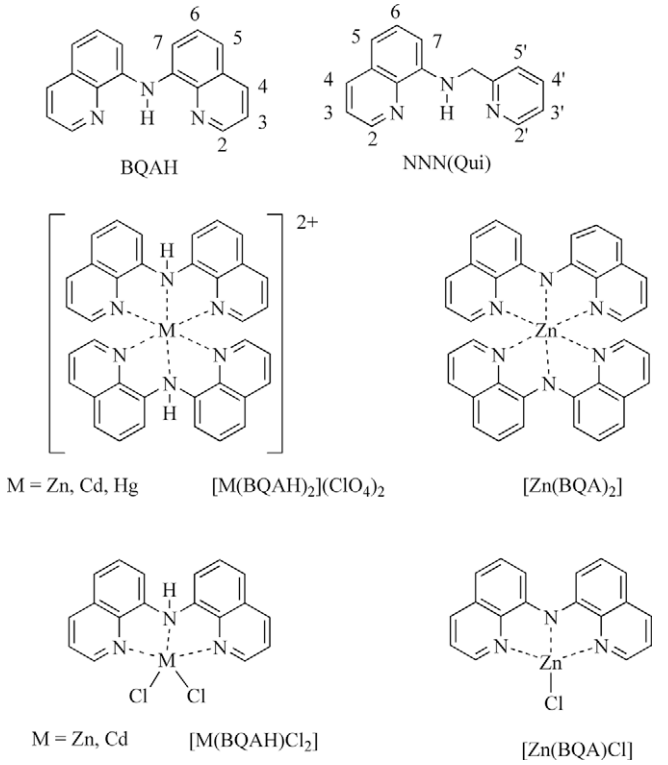



**Scheme 1.** Ligands and complexes synthesized and studied.

It is noteworthy that the aminic proton of the ligand BQAH assumes a considerable acidic character when coordinated to cationic metals. It is therefore possible to isolate hexacoordinate cationic $[M(BQAH)_2]^{2+}$ and neutral $[M(BQA)_2]$ derivatives bearing the protonated or deprotonated ligand. The pentacoordinate derivatives of BQAH and the tetracoordinate [Zn(BQA)Cl] were also synthesized.

## 2. Experimental

### 2.1. Solvents and reagents

$CH_3CN$, DMSO (dimethylsulfoxide), $CH_3OH$, $C_2H_5OH$, butan-2-ol, ethylene-glycol, $H_2SO_4$ and TEA (triethylamine), were commercial grade chemicals and were used without further purification. $CH_2Cl_2$ was distilled over $CaH_2$, toluene and THF were distilled over Na/benzophenone. $Hg(ClO_4)_2{\cdot}6H_2O$, $Cd(ClO_4)_2{\cdot}6H_2O$ (Alfa-Aesar), $Zn(ClO_4)_2{\cdot}6H_2O$, $HgCl_2$, $CdCl_2{\cdot}H_2O$, $ZnCl_2$ (Sigma–Aldrich), $CD_3Cl$, $CD_3CN$ and DMSO-$d^6$ are commercial grade reagents and were used as purchased.

### 2.2. IR, NMR, UV–Vis absorption and fluorescence measurements

IR, $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer and on a Bruker Avance 300 spectrometer, respectively. The proton and carbon assignment was performed by $^1H$–$^{13}C$-HMQC and HMBC techniques in the case of the bis-chelate complexes $[ML_2](ClO_4)_2$ (M = Zn, Cd, Hg; L = BQAH) and of the complex [Zn(BQA)Cl] in $CD_3CN$ and $CDCl_3$, respectively. The proton assignment for the complexes $[Zn(BQA)_2]$ and $[M(BQAH)Cl_2]$ (M = Zn, Cd) was obtained by $^1H$–$^1H$-COSY experiment due to their low solubility in DMSO and $CD_3CN$, respectively. UV–Vis spectra were taken on a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Perkin–Elmer PTP6 (Peltier temperature programmer) apparatus. All corrected fluorescence spectra were recorded on a Perkin–Elmer luminescence spectrometer LS 50 ($T$ = 298 K) and the fluorescence quantum yields $Q_X$ were measured relative to quinine sulfate in $H_2SO_4$ 0.5 M as a standard and calculated according to the formula:

$$Q_X = Q_{ST}\frac{S_X}{S_{ST}}\cdot\frac{A_{ST}}{A_X}\cdot\frac{n_X^2}{n_{ST}^2}$$

where $S$ represents the area of the corrected emission fluorescence spectra ($\lambda_{exc}$ = 320 nm), $A$ is the optical density at 320 nm and $n$ is the refractive index of the solvent used.

### 2.3. Synthesis of ligands

#### 2.3.1. BQAH

The synthesis of the ligand BQAH was performed according to Buckwald's protocol based on the catalyzed coupling between 8-aminoquinoline and 8-bromoquinoline [5].

To a stirred suspension of $Pd_2DBA_3$ (176 mg, 0.192 mmol) and racemic BINAP (239 mg, 0.384 mmol) in 30 ml of anhydrous toluene under inert atmosphere ($N_2$), 8-bromoquinoline (2.00 g, 9.61 mmol), 8-amino-quinoline (1.39 g, 9.64 mmol) and 70 ml of anhydrous toluene were added. Then, NaO*t*-Bu (1.11 g, 11.5 mmol) was introduced and the resulting mixture was stirred at 110 °C for three days. The solution was filtered at R.T. on silica gel and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using $Et_2O$:$CH_2Cl_2$ (1:10) as eluent to give the title product as orange microcrystals (1.95 g, 75%).

IR (KBr pellet): $\nu_{N-H}$ 3286 $cm^{-1}$.

$^1H$ NMR ($CD_3CN$, $T$ = 298 K, ppm): amine protons, $\delta$, 10.98 (br s, 1H, N*H*), quinoline protons 7.44 (dd, 1H, $H^7$, $J$ = 8.1, 1.8 Hz), 7.60 (t, 1H, $H^6$, $J$ = 8.1 Hz), 7.60 (dd, 2H, $H^3$, $J$ = 8.1, 4.2 Hz), 7.96 (dd, 1H, $H^5$), 8.31 (dd, 1H, $H^4$, $J$ = 1.8, 8.1 Hz), 8.95 (dd, 1H, $H^2$, $J$ = 4.2 Hz).

#### 2.3.2. NNN(Qui)

The title ligand was synthesized according to a published method [4].

### 2.4. Synthesis of bis-chelate complexes

#### 2.4.1. $[Hg(BQAH)_2](ClO_4)_2$

Solid $Hg(ClO_4)_2{\cdot}5H_2O$ (52.6 mg, 0.11 mmol) was added to a stirred solution of BQAH (58.9 mg, 0.22 mmol) in 5 ml of $CH_2Cl_2$. The reaction proceeded in heterogeneous phase for 30 min with the gradual separation of the title compound as a yellow precipitate. The complex was filtered off and washed with $Et_2O$, toluene and *n*-hexane and dried under vacuum to give yellow microcrystals (86.4 mg, 85%).

IR (KBr pellet, $cm^{-1}$): $\nu_{N-H}$ 3211, $\nu_{C-H}$ 3054, 2958, $\nu_{C=N}$ 1615, 1592, $\nu_{C=C}$ 1530, 1499, $\nu_{ClO_4}$ 1111, 1077.

$^1H$ NMR ($CD_3CN$, $T$ = 298 K, ppm): quinoline protons, $\delta$, 7.58–7.62 (m, 12H, $H^6$, $H^7$, $H^3$), 7.84 (br t, 4H, $H^5$, $J$ = 4.2 Hz), 8.46 (br d, 4H, $H^4$, $J$ = 8.4 Hz), 8.64 (br d, 4H, $H^2$, $J$ = 2.4 Hz).

$^{13}C$ NMR ($CD_3CN$, $T$ = 298 K, ppm): quinoline carbons, $\delta$, 122.6 ($C^3$), 125.9 ($C^{10}$), 126.2 ($C^7$), 127.8 ($C^5$), 129.5 ($C^6$), 138 ($C^8$), 139.4 ($C^4$), 140.3 ($C^9$), 150.9 ($C^2$).

*Anal.* Calc. for $C_{36}H_{26}HgCl_2N_6O_8$: C, 45.89; H, 2.78; N, 8.92. Found: C, 45.94; H, 2.71; N, 9.01%.

The following complexes were synthesized in an analogous way using the appropriate perchlorate salts.

#### 2.4.2. $[Cd(BQAH)_2](ClO_4)_2$

Yield 98% (gray microcrystals).

IR (KBr pellet, $cm^{-1}$): $\nu_{N-H}$ 3230, $\nu_{C-H}$ 3071, 2958, 2919, $\nu_{C=N}$ 1620, 1596, 1569, $\nu_{C=C}$ 1530, 1508, $\nu_{ClO_4}$1099.

$^1$H NMR ($CD_3CN$, $T$ = 298 K, ppm): amine protons, $\delta$, 7.51 (br s, 2H, N*H*), quinoline protons 7.56–7.63 (m, 8H, $H^6$, $H^3$), 7.76 (d, 4H, $H^7$, $J$ = 7.2 Hz), 7.84 (d, 4H, $H^5$, $J$ = 8.1 Hz), 8.45 (dd, 4H, $H^4$, $J$ = 8.4, 1.2 Hz), 8.72 (d, 4H, $H^2$, $J$ = 3.9 Hz).

$^{13}$C NMR ($CD_3CN$, $T$ = 298 K, ppm): quinoline carbons, $\delta$, 122.6 ($C^3$), 126.2 ($C^{10}$), 126.5 ($C^7$), 127.5 ($C^5$), 129.1 ($C^6$), 138.8 ($C^8$), 139.7 ($C^4$), 140.6 ($C^9$), 150.7 ($C^2$).

*Anal.* Calc. for $C_{36}H_{26}CdCl_2N_6O_8$: C, 50.63; H, 3.07; N, 9.84. Found: C, 50.74; H, 2.98; N, 9.85%.

#### 2.4.3. [Zn(BQAH)$_2$](ClO$_4$)$_2$

Yield 62% (pink microcrystals).

IR (KBr pellet, cm$^{-1}$): $\nu_{N-H}$ 3204, $\nu_{C-H}$ 3072, 2969, $\nu_{C=N}$ 1623, $\nu_{C=C}$ 1531, 1509, $\nu_{ClO_4}$ 1109, 1089.

$^1$H NMR ($CD_3CN$, $T$ = 333 K, ppm): quinoline protons, $\delta$, 7.63 (dd, 4H, $H^3$, $J$ = 8.2, 1.5 Hz), 7.69 (t, 4H, $H^6$, $J$ = 7.8 Hz), 7.89 (d, 4H, $H^7$, $J$ = 8.1 Hz), 8.00 (d, 4H, $H^5$, $J$ = 6.9 Hz), 8.51 (dd, 4H, $H^4$, $J$ = 8.2, 1.5 Hz), 8.74 (d, 4H, $H^2$, $J$ = 3.3 Hz).

$^{13}$C NMR ($CD_3CN$, $T$ = 333 K, ppm): quinoline carbons, $\delta$, 122.6 ($C^3$), 126.3 ($C^{10}$, $C^7$), 128 ($C^5$), 129.4 ($C^6$), 139.3 ($C^8$), 139.9 ($C^4$), 140.5 ($C^9$), 149.6 ($C^2$).

*Anal.* Calc. for $C_{36}H_{26}ZnCl_2N_6O_8$: C, 53.58; H, 3.25; N, 8.79. Found: C, 53.77; H, 3.18; N, 8.83%.

#### 2.4.4. [Zn(BQA)$_2$]

The preparation of the title complex was different from the synthesis reported in the literature [6]; the spectroscopic data were however coincident.

To 0.100 g (0.37 mmol) of BQAH and 0.103 g (0.74 mmol) of triethylamine dissolved in 5 ml of anhydrous THF, a solution of 0.0686 g (0.18 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 5 ml of THF was added dropwise under inert atmosphere (Ar). The red complex which precipitated from the reaction mixture was stirred for 1 h at R.T., filtered off (G3), washed with EtOH, $Et_2O$, and pentane and dried under vacuum. As a result 0.095 g (0.18 mmol) of red microcrystals was obtained (yield 85%).

IR (KBr pellet, cm$^{-1}$): $\nu_{C-H}$ 3040, $\nu_{C=N}$ 1556, $\nu_{C=C}$ 1492, 1448, 1394.

$^1$H NMR ($CDCl_3$, $T$ = 298 K, ppm): quinoline protons, $\delta$, 6.95–7.00 (m, 4H, $H^6$, $H^7$), 7.61 (t, 2H, $H^3$, $J$ = 7.7 Hz), 7.93 (dd, 2H, $H^5$, $J$ = 8.1, 1.5 Hz), 8.01 (dd, 2H, $H^4$, $J$ = 4.2, 1.5 Hz), 8.21 (d, 2H, $H^2$, $J$ = 7.7 Hz).

### 2.5. Synthesis of mono-chelate complexes

#### 2.5.1. [Cd(BQAH)Cl$_2$]

To a stirred solution of 0.0644 g (0.24 mmol) of BQAH in 5 ml of $CH_2Cl_2$, 0.0455 g (0.23 mmol) of solid $CdCl_2$ was added. The reaction proceeds in heterogeneous phase for 30 min with the gradual separation of the title compound as a white precipitate. The complex was filtered off (G3) and washed with $CH_2Cl_2$, $Et_2O$ and *n*-hexane and dried under vacuum. As a result 0.0652 g (0.16 mmol) of white microcrystals was obtained (yield 69%).

IR (KBr pellet, cm$^{-1}$): $\nu_{N-H}$ 3193, $\nu_{C-H}$ 3050, $\nu_{C=N}$ 1619, 1595, $\nu_{C=C}$ 1507, 1472.

$^1$H NMR ($CD_3CN$, $T$ = 333 K, ppm): quinoline protons, $\delta$, 7.68 (m, 6H, $H^3$, $H^7$, $H^6$), 7.98 (t, 4H, $H^5$, $J$ = 4.2 Hz), 8.43 (dd, 2H, $H^4$, $J$ = 8.4, 1.5 Hz), 9.03 (dd, 2H, $H^2$, $J$ = 4.2, 1.5 Hz).

*Anal.* Calc. for $C_{18}H_{13}CdCl_2N_3$: C, 47.55; H, 2.88; N, 9.24. Found: C, 47.81; H, 2.78; N, 9.29%.

The following complex was synthesized in an analogous way using $ZnCl_2$.

#### 2.5.2. [Zn(BQAH)Cl$_2$]

Yield 84% (yellow microcrystals).

IR (KBr pellet, cm$^{-1}$): $\nu_{N-H}$ 3183, $\nu_{C-H}$ 3065, 2919, 2846, $\nu_{C=N}$ 1615, $\nu_{C=C}$ 1507, 1470.

$^1$H NMR ($CD_3CN$, $T$ = 333 K, ppm): quinoline protons, $\delta$, 7.75 (m, 6H, $H^3$, $H^7$, $H^6$), 8.08 (bd, 4H, $H^5$, $J$ = 0.9 Hz), 8.50 (bd, 2H, $H^4$, $J$ = 0.9 Hz), 9.22 (br s, 2H, $H^2$).

*Anal.* Calc. for $C_{18}H_{13}CdCl_2N_3$: C, 53.04; H, 3.21; N, 10.31. Found: C, 53.11; H, 3.12; N, 10.42%.

#### 2.5.3. [Zn(BQA)Cl]

To BQAH (100 mg, 0.37 mmol) and triethylamine (103 mg, 0.74 mmol) dissolved in 5 ml of anhydrous THF, a solution of $ZnCl_2$ (50 mg, 0.37 mmol) in 5 ml of THF was added dropwise under inert atmosphere (Ar). The red complex precipitated from the reaction mixture. After stirring for 1 h at R.T., the reaction product was filtered off, washed with $CH_2Cl_2$, $Et_2O$, and pentane and dried under vacuum. Red microcrystals of the title compound were obtained (96.8 mg, 69%).

IR (KBr pellet, cm$^{-1}$): $\nu_{C-H}$ 3044, $\nu_{C=N}$ 1565, $\nu_{C=C}$ 1496, 1460, 1401.

$^1$H NMR (DMSO-$d^6$, $T$ = 298 K, ppm): quinoline protons, $\delta$, 7.18 (d, 2H, $H^7$, $J$ = 7.8 Hz), 7.55 (t, 2H, $H^6$, $J$ = 7.8 Hz), 7.73 (dd, 2H, $H^3$, $J$ = 8.3, 4.3 Hz), 7.86 (d, 2H, $H^5$, $J$ = 7.8 Hz), 8.45 (dd, 4H, $H^4$, $J$ = 8.3, 1.5 Hz), 8.84 (dd, 4H, $H^2$, $J$ = 4.3, 1.5 Hz).

$^{13}$C NMR (DMSO-$d^6$, $T$ = 298 K, ppm): quinoline carbons, $\delta$, 110.2 ($C^5$), 113.1 ($C^7$), 122.25 ($C^3$), 129.48 ($C^6$), 129.7 ($C^{10}$), 139.1 ($C^4$), 140.1 ($C^9$), 144.1 ($C^8$), 146 ($C^2$).

*Anal.* Calc. for $C_{18}H_{12}ZnClN_3$: C, 58.25; H, 3.26; N, 11.32. Found: C, 58.31; H, 3.17; N, 11.41%.

### 2.6. Spectrophotometric determination of formation constants of the complexes

All determinations of formation constants were carried out in anhydrous $CH_3CN$ at 25 °C. The mother solutions of the ligands NNN(Qui) and BQAH (50 ml, $1 \times 10^{-3}$ mol dm$^{-3}$) and those of the titrant perchlorate salts $M(ClO_4)_2$ ([$M(ClO_4)_2$] = 0.01 mol dm$^{-3}$ (Zn, Hg), 0.05 mol dm$^{-3}$ (Cd)) were prepared by dissolving the appropriate weighed amount of the ligand or salt in a volumetric flask and diluting to the mark with anhydrous $CH_3CN$.

The titration experiments were carried out by titrating the solutions of the ligand prepared by diluting the mother solution to the appropriate concentration ($1 \times 10^{-4}$ mol dm$^{-3}$) with microaliquots of the mother solutions of the metal perchlorates by means of a suitable micropipette. The ensuing absorbance values at different wavelengths were recorded at 25 °C and the evaluation of stepwise stability constants from the absorbance versus volume of $M(ClO_4)_2$ ml data was achieved by the program HYPERQUAD™ [7]. The expected total absorbance value ($A_T$) for each solution is given as $A_T = \Sigma_i \varepsilon_i c_i$, were $\varepsilon_i$ and $c_i$ are the molar extinction coefficients and the concentrations of the involved species. The iterative adjustment of calculated values of $\varepsilon_{ML}$ and $\varepsilon_{ML2}$ and the subsequent refinement of the parameters was continued until the correlation matrix was minimized. The refined $\varepsilon_L$ values are in good agreement with those measured for an independently synthesized authentic sample.

### 2.7. Spectrometric determination (NMR) of the formation constants of the complexes

All the experiments were carried out at 25 °C in $CD_3CN$ ($D_2O$ < 0.05%). To 0.5 ml of a solution of the ligand NNN(Qui) or BQAH ([Ligand] = 0.05 mol dm$^{-3}$) in a NMR test tube microaliquots of a solution of $Hg(ClO_4)_2$ ([$Hg(ClO_4)_2$] = 0.1 mol dm$^{-3}$) were added using a micropipette. The chemical shifts of the quinoline protons $H^2$ and $H^4$ were interpolated as a function of the volume of the added titrant by means of the HYPNMR2004 program [7]. The ensuing formation constants were in agreement with the values independently determined in the case of the analogous spectrophotometric determination.

**Table 1**
Absorption maxima (nm) for the ligands Quinoline, 8-amino-quinoline, NNN(Qui) and BQAH in aprotic and protics (*italics*) solvents. The underlined values correspond to the Franck–Condon transitions, (s) indicates shoulder, * indicates vibration structure.

| | Quinoline | 8-Amino-quinoline | NNN(Qui) | BQAH |
|---|---|---|---|---|
| *n*-Hexane | | (332 s), 346 | (336 s), 365 | (339 s), (395/409)* |
| Dichloromethane | | (337 s), 345 | (336 s), 363 | (339 s), 404 |
| Acetone | | (337 s), 348 | (336 s), 363 | (339 s), 400 |
| Acetonitrile | (300/313)* | (337 s), 345 | (336 s), 360 | (339 s), 396, 480 |
| *Ethanol* | | 338, (350 s) | (336 s), 358 | (339 s), 400, 480 |
| *Methanol* | | 337 | (336 s), 358 | (339 s), 400, 480 |
| *Water* | (291/313)* | 332 | (336 s), 365 | – |

### 2.8. Spectrofluorimetric characterization of the complexes

The spectrofluorimetric characterization of the complexes was carried out in anhydrous $CH_3CN$ at 25 °C. The mother solutions of the ligands BQAH and NNN(Qui) (50 ml, $1 \times 10^{-4}$ mol dm$^{-3}$) and of the perchlorate salts $M(ClO_4)_2$ ($[M(ClO_4)_2] = 0.005$ mol dm$^{-3}$ (Zn, Hg), 0.01 mol dm$^{-3}$ (Cd)) were prepared at 25 °C by dissolving the appropriate weighed amount of the ligand or salt in a volumetric flask and diluting to the mark with anhydrous $CH_3CN$. The mother solutions of the ligands were diluted to the appropriate concentration ($3 \times 10^{-5}$ mol dm$^{-3}$ in the case of BQAH and $4.3 \times 10^{-5}$ mol dm$^{-3}$ in the case of NNN(Qui)) and microaliquots of the perchlorate salt solutions were added by means of a micropipette. The ensuing fluorescence spectra turned out to be coincident with the spectra of authentic samples of the complexes in $CH_3CN$.

**Table 2**
Fluorescence maxima (nm) and fluorescence quantum yields $Q_F$ (in parenthesis) for the ligands 8-amino-quinoline, NNN(Qui) and BQAH in aprotic and protic (*italics*) solvents.

| | ET(30) | 8-Amino-quinoline $\lambda_{exc}$ 345 nm | NNN(Qui) $\lambda_{exc}$ 360 nm | BQAH $\lambda_{exc}$ 400 nm |
|---|---|---|---|---|
| *n*-Hexane | 30.9 | 426 (0.011) | 426 (0.001) | 432 (0.005) |
| Dichloromethane | 41.1 | 466 (0.039) | 468 (0.014) | 469 (0.003) |
| Acetone | 42.2 | 467 (0.044) | 472 (0.016) | 472 (0.002) |
| Acetonitrile | 46.0 | 473 (0.053) | 475 (0.020) | 477 (0.002) |
| *2-Propanol* | *48.4* | *455 (<0.001)* | *553 (0.002)* | *456 (0.002)* |
| *Ethanol* | *51.9* | *455 (<0.001)* | *507 (0.004)* | *458 (0.001)* |
| *Ethylene-glycol* | *53.8* | *463 (<0.001)* | *473 (0.005)* | *456 (0.001)* |
| *Methanol* | *55.5* | *465 (<0.001)* | *458 (0.006)* | *456 (<0.001)* |
| *Water* | *62.8* | *500 (<0.001)* | – | – |

## 3. Result and discussion

### 3.1. General remarks

Owing to the very low solubility of the ligand BQAH and of the related complexes in water we have determined the formation constants of the complexes in $CH_3CN$. In order to compare the behavior of BQAH with that of the ligands previously studied [4] we have re-determined the formation constants of the zinc triad metals with the ligand NNN(Qui) in $CH_3CN$.

The higher solubility of ligands and complexes in such solvent allows the determination of the formation constants by means of different approaches, i.e. UV–Vis and NMR techniques, thereby providing an unambiguous test of internal consistency.

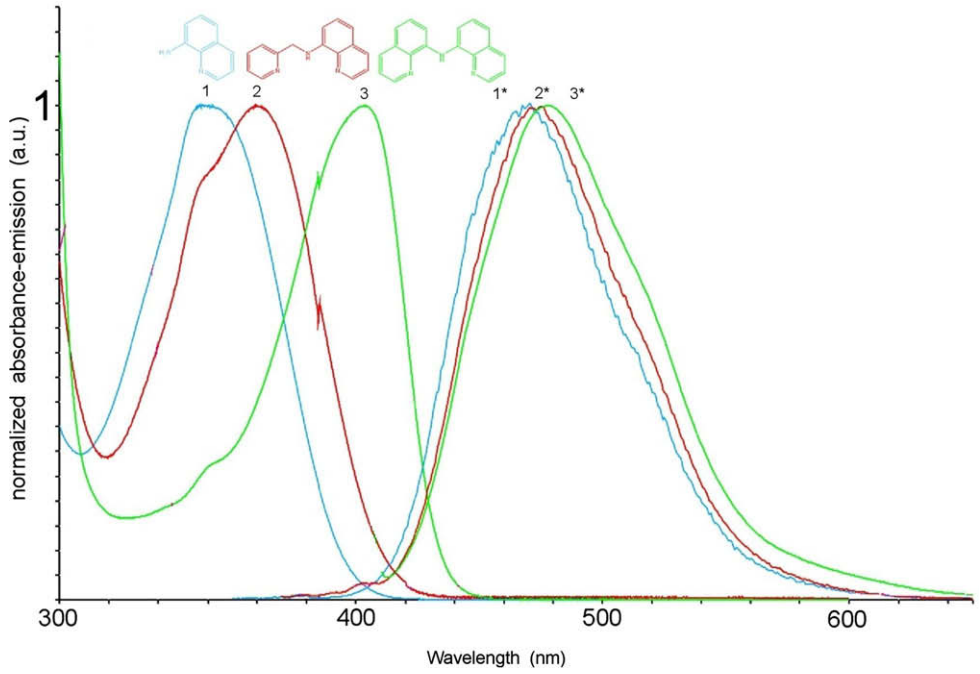



**Fig. 1.** Normalized absorption and fluorescence spectra of the ligands 8-aminoquinoline (1, 1* blue), NNN(Qui) (2, 2* red) and BQAH (3, 3* green) in acetonitrile. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

However, the complete assignment of the proton signals is not always possible. For instance, owing to the acidity of the coordinated amine and the low solubility of the mono-chelate compounds the aminic proton signals are seldom detectable.

### 3.2. Synthesis of the complexes

#### 3.2.1. Bis-chelate complexes

Addition of the perchlorate salt $M(ClO_4)_2$ (M = Zn, Cd, Hg) to the ligand BQAH in $CH_2Cl_2$ yields the corresponding complexes of general formula $[M(BQAH)_2](ClO_4)_2$.

The most prominent aspect of the $^1H$ NMR spectra of the ensuing complexes in $CD_3CN$ is represented by the high-field shift of the $H^2$ quinoline protons upon coordination. Such a behavior, which is not unprecedented, was already discussed in previous works and was traced back to the anisotropic shielding of the $H^2$ protons due to the π-delocalized electrons of the close aromatic rings belonging to the opposite ligand [4,8]. However, at variance with the $^1H$ NMR spectra of the complexes published elsewhere [4] and with that of the comparable species $[Zn(NNN(Qui))_2]^{2+}$ the BQAH derivatives display a marked broadening of the aromatic signals which we tentatively ascribe to the presence of a fast acid–base equilibrium between the protonated substrate $[M(BQAH)_2]^{2+}$ and its de-protonated counterpart $[M(BQA)_2]$ (see Scheme 1). As a matter of fact, the $^1H$ NMR in $CD_2Cl_2$ of an authentic sample of the complex $[Zn(BQA)_2]$ independently synthesized gives no hints of signal broadening and all the signals are well resolved owing to the ligand inability to exchange protons in this solvent. Unfortunately, the obvious countercheck is impossible due to the almost complete insolubility of the protonated species $[Zn(BQAH)_2]^{2+}$ in $CD_2Cl_2$.

#### 3.2.2. Mono-chelate complexes

Addition of the chloride salt $MCl_2$ (M = Zn, Cd) to the ligand BQAH in $CH_2Cl_2$ yields the corresponding complexes of general formula $[M(BQAH)Cl_2]$. The presence of chloride in solution severely hampers the formation of the mono-chelate Hg derivatives. This effect was already noticed with different ligands; probably in such a solvent the formation of chain $HgCl_2$ complexes is favored. Conversely, the synthesis of $[Hg(NNN)Cl_2]$ complexes in water is possible [4].

Since no anisotropic shielding is possible in the case of mono-chelate complexes owing to the absence of the opposite ligand, the $H^2$ signal undergoes a predictable low-field shift upon coordination. In the case of the complex $[Zn(BQAH)Cl_2]$ the $H^2$ signal broadening suggests the presence of both protonated and deprotonated aminic nitrogen in a fast acid–base equilibrium. The spectrum in DMSO-$d^6$ of the almost insoluble and independently synthesized [Zn(BQA)Cl] complex displays sharp signals and a high-field shift of the $H^2$ protons. In this case, however, the chemical shift of the $H^2$ protons cannot be used as a test of mono-coordination. Comparison with the complexes of the X group with the same BQA ligand shows the utter unpredictability of the resonance position of that signal which can be shielded, isochronous or deshielded with respect to the signal of the uncoordinated ligand in the case of Ni, Pd and Pt, respectively [5].

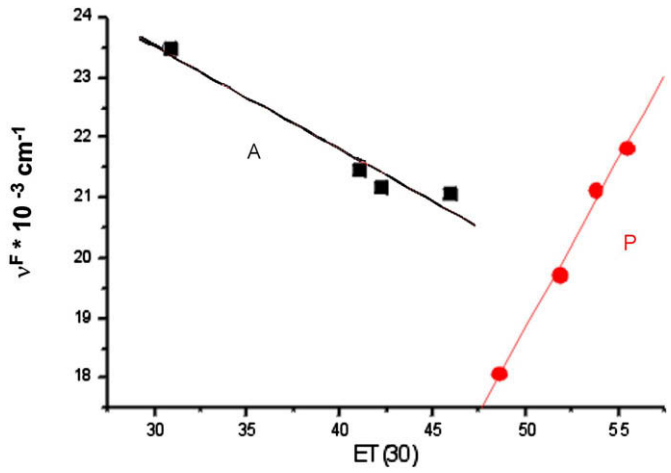



**Fig. 2a.** Linear correlations between the energy of the fluorescence maxima $\nu_F$ and the ET(30) constant of the solvent in the case of NNN(Qui). A – aprotic solvents, P – protic solvents.

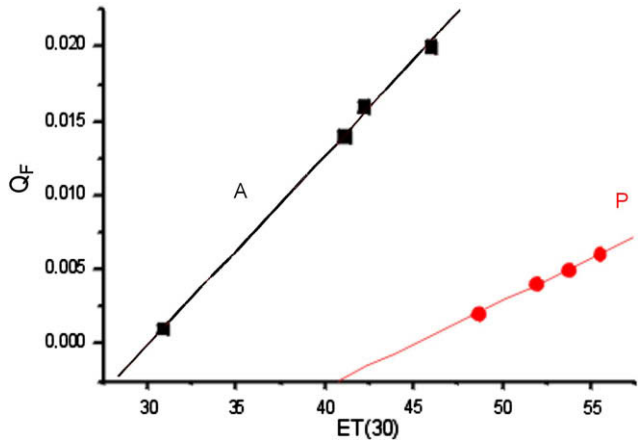



**Fig. 2b.** Linear correlations between the fluorescence quantum yield $Q_F$ and the ET(30) constant of the solvent in the case of NNN(Qui). A – aprotic solvents, P – protic solvents.

### 3.3. Photophysical properties of the ligands

#### 3.3.1. UV–Vis absorption spectra

In Table 1, the maxima of the longest-wavelength absorption band of the ligands in solvents of different polarity are presented. Typically, the Franck–Condon absorption transitions shift bathochromically with increasing size of the π-electronic conjugated system. On the other hand, for all ligands no effect of the polarity of the media is observed, which points to negligible changes in the dipole moment upon excitation.

#### 3.3.2. Fluorescence spectra

The maxima of the fluorescence bands of the ligands in solvents with different polarity and proton ability upon excitation at the corresponding absorption maximum are reported in Table 2 together with the ET(30) constant of the solvent [9] and the calculated fluorescence quantum yield values $Q_F$.

In Fig. 1, the normalized absorption and fluorescence spectra of the ligands in acetonitrile are presented.

The analysis of the experimental data in Table 2 shows that the dependencies $\nu_F$/ET(30) and $Q_F$/ET(30) in protic and non-protic solvents are described by two different linear correlations.[1] Fig. 2a and b illustrates the cases for NNN(Qui) ligand. Similar to the conclusions in [10] these results are to be attributed to the different nature of the emitting states of the ligands in protic and non-protic solvents, due

[1] The very low quantum yields of the ligand BQAH do not allow the correlation of $Q_f$ with the ET(30) parameter. The similarity of the behaviour in solution between the ligands BQAH and NNN(Qui) and the correlation between the energy of the absorbance maxima and ET(30) parameters for the ligand BQAH are however a clear indication that similar phenomena take place in both cases.

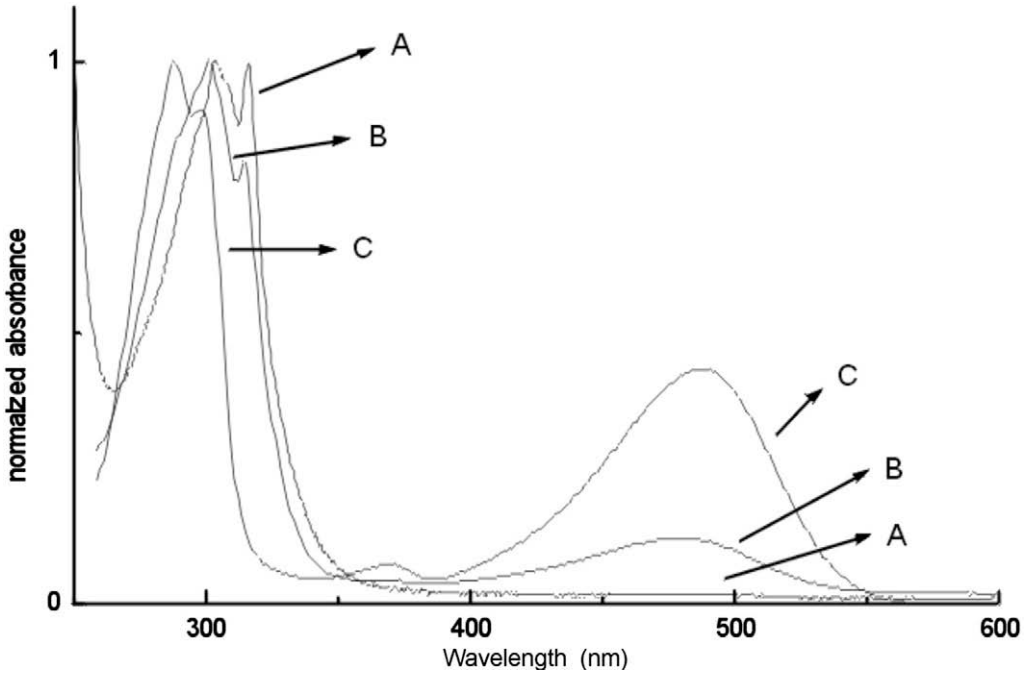



**Fig. 3.** Absorption spectra of the complex $[Zn(BQAH)Cl_2]$ ($[[Zn(BQAH)Cl_2]] \approx 1 \times 10^{-4}$ mol dm$^{-3}$) in: (A) $CH_2Cl_2$, (B) $CH_3CN$ and (C) $CH_3OH$.

**Table 3**
Absorbance maxima (nm) for the mono- and bis-chelate complexes in dichloromethane, acetonitrile and methanol; the underlined values correspond to the maxima, * indicates vibration structure, TD – complex totally dissociated, empty cells indicate no synthesized complexes.

| | $[M(NNN(Qui))_2](ClO_4)_2$ | $[M(NNN(Qui))Cl_2]$ | $[M(BQAH)_2](ClO_4)_2$ | $[M(BQAH)Cl_2]$ | $[M(BQA)_2]$ | $[M(BQA)Cl]$ |
|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | Zn *(302, 316)**<br>Cd *(302, 316)**<br>Hg *(302, 316)** | Zn *(302, 316)**<br>Cd *(302, 316)**<br>Hg *(302, 316)** | Zn *(302, 316)**<br>Cd *(302, 316)**<br>Hg *(302, 316)** | Zn *(302, 316)**<br>Cd *(302, 316)** | Zn *(290/300)**, *370*, *503* | Zn *(290/300)**, *370*, *490* |
| $CH_3CN$ | Zn *(302, 316)**<br>Cd *(302, 316)**<br>Hg *(302, 316)** | Zn *(302, 316)**<br>Cd *(302, 316)**<br>Hg *(302, 316)** | Zn *(302, 316)**, *(480)*<br>Cd *TD*<br>Hg *TD* | Zn *(302, 316)**, *(480)*<br>Cd *TD* | Zn *(290/300)**, *370*, *497* | Zn *(290/300)**, *370*, *485* |
| $CH_3OH$ | Zn *(302, 316)**<br>Cd *(302, 316)**<br>Hg *(302, 316)** | Zn *(302, 316)**<br>Cd *(302, 316)**<br>Hg *TD* | Zn *493*<br>Cd *TD*<br>Hg *TD* | Zn *(290/300)**, *370*, *493*<br>Cd *(290/300)**, *370*, *493* | Zn *(290/300)**, *370*, *493* | Zn *(290/300)**, *370*, *492* |

to the formation of inter-molecular hydrogen bonds with the protic solvents in the singlet excited state of the compounds.

### 3.4. Photophysical properties of the complexes

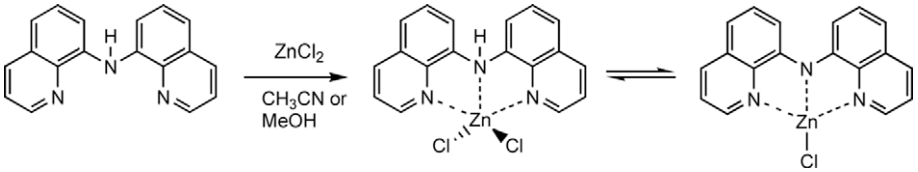
#### 3.4.1. UV–Vis absorption

The energy and shape of the absorption bands of mono- and bis-chelate complexes of the NNN(Qui) ligand are practically independent of the polarity of the solvent and the metal. The absorption band has clearly a vibrational structure at 302 and 316 nm (Table 2, Fig. 3). Similar spectral behavior is observed also for $[M(BQAH)_2](ClO_4)_2$ and $[M(BQAH)Cl_2]$ in dichloromethane. The Franck–Condon absorption transitions of these chelate complexes in $CH_2Cl_2$ are hypsochromically shifted by 4630 cm$^{-1}$ for NNN(Qui) and by 7260 cm$^{-1}$ in the case of BQAH in comparison to the corresponding free ligands. If we bear in mind the structure of the complexes, this result should be attributed to the breaking of the conjugation between the two aromatic rings in the complexes, originally mediated by the aminic nitrogen lone pair.

In the remaining cases, a new absorption band around 500 nm is observed in the absorption spectra of the complexes, and in some cases this long-wavelength band dominates the whole spectrum (see Table 3 and Fig. 3).

We suggest that the following equilibrium involving protonated and deprotonated forms takes place in the solutions of the complexes (Scheme 2).

In this scheme the absorption band at 500 nm is to be reasonably related to the deprotonated form, because the independently




**Scheme 2.** Acid-base equilibrium for the complex $[Zn(BQAH)Cl_2]$ in the solvents MeCN and MeOH.

**Table 4**
Fluorescence maxima (nm) and fluorescence quantum yields (in bold) of the complexes. NF - complex does not fluoresce; TD – complex totally dissociated; (s) – shoulder; * – the ensuing fluorescence quantum yield is reduced by partial dissociation of the complex; # – $\lambda_{exc}$ 490 nm, in the other case $\lambda_{exc}$ 316 nm. Empty cells indicate no synthesized complexes.

| | | $[M(NNN(Qui))_2](ClO_4)_2$ | $[M(NNN(Qui))Cl_2]$ | $[M(BQAH)_2](ClO_4)_2$ | $[M(BQAH)Cl_2]$ | $[M(BQA)_2]$ | [M(BQA)Cl] |
|---|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | Zn | *(495 s)*, *516* **0.034** | *485*, *(520 s)* **0.039** | *526* **0.010** | *(485 s)*, *520* **<0.001** | *595*# **<0.001** | *603*# **<0.001** |
| | Cd | *(485 s)*, *520* **0.015*** | *485*, *(520 s)* **0.040** | *526* **0.005*** | *520* **<0.001** | | |
| | Hg | NF | *472* **<0.001** | *523* **<0.001** | | | |
| $CH_3CN$ | Zn | *520* **0.034** | *520* **0.044** | *370*, *433*, *520* | *370*, *433*, *520* | *605*# **<0.001** | *605*# **<0.001** |
| | Cd | *520* **0.015*** | *520* **0.045** | TD | TD | | |
| | Hg | NF | NF | TD | | | |
| $CH_3OH$ | Zn | *518* **0.025** | *520* **0.044** | 600* **<0.001** | *600*# **<0.001** | *602*# **<0.001** | *602*# **<0.001** |
| | Cd | *520* **0.010*** | *520* **0.043** | TD | *595*# **<0.001** | | |
| | Hg | NF | TD | | | | |

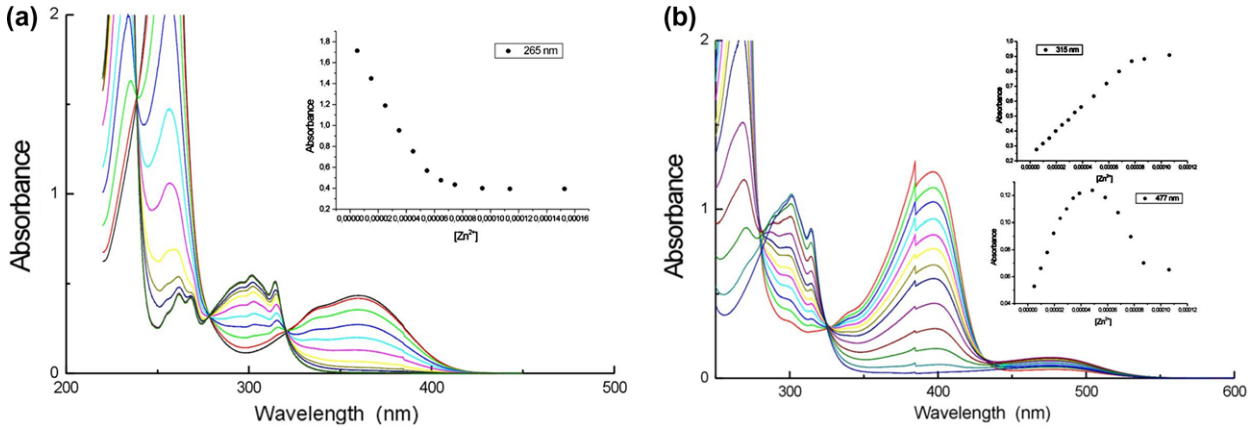



**Fig. 4.** Absorbance changes upon addition of $Zn(ClO_4)_2$ to an acetonitrile solution of NNN(Qui) (a) and BQAH (b) ([Ligand] = $1 \times 10^{-4}$ mol dm$^{-3}$).

synthesized and characterized complex [Zn(BQA)Cl] (obtained by reacting the ligand BQAH with $ZnCl_2$ in the presence of triethylamine, see Section 2) has the same spectral characteristics. Depending on the structure of the ligand, the metal and the properties of the solvent the equilibrium is preferentially shifted to one of these two forms, thereby changing the relative intensity of the two bands in the absorption spectrum of the complexes (Table 3, Fig. 3).

### 3.4.2. Fluorescence

The fluorescence FC transitions (nm) and fluorescence quantum yields (in bold) of the complexes in $CH_2Cl_2$, $CH_3CN$ and $CH_3OH$ are presented in Table 4.

The comparison of the experimental data shows that the highest fluorescence quantum yields are observed for the complex $[M(NNN(Qui))Cl_2]$.[2] In this case, the quantum yields of Zn and Cd complexes are almost the same, while the presence of Hg totally extinguishes the emission. Conversely, when the bis-chelate complexes $[M(NNN(Qui))_2](ClO_4)_2$ and $[M(BQAH)_2](ClO_4)_2$ are considered, probably partial dissociation of the cadmium reduces the quantum yield. However, the emission of the cadmium complexes is somehow reduced by partial dissociation of the bis-chelate complexes in solution. Again, Hg totally extinguishes the emission. The quenching effect of the heavy mercury metal is due to the efficient spin–orbital interaction, which increases the intersystem crossing probability, thus enhancing the nonradiative deactivation of the fluorescent S1($\pi\pi^*$) state.

The fluorescence maxima of the complexes are always bathochromically shifted toward the corresponding ligand in the same solvent, indicating the lengthening of the conjugated π-electronic system in the complexes as compared with the respective ligands.

In all cases, when the longest wavelength band in the absorption spectrum of the complex is in the region of 500 nm, i.e. the ground state is connected to the deprotonated form (Table 3), the Stoke shifts $\Delta\nu^{ST} = \nu^{ABS} - \nu^{FL}$ do not exceed 4000 cm$^{-1}$, which is the normal value for conjugated organic compounds. However, for all protonated forms of the complexes, which are characterized by only one absorption band in the spectral region of 320 nm, the Stoke shifts are very large – about 12 000 cm$^{-1}$, see for instance the cases of $[M(NNN(Qui))_2](ClO_4)_2$ and $[M(NNN(Qui))Cl_2]$, Tables 3 and 4. Such abnormally high values of the Stoke shift indicate structural, not only geometrical changes in the first singlet excited state of the molecule as compared to the ground state.

Our hypothesis is that the excitation of the complexes, which in the ground state are in their protonated form, leads to crucial reorganization of their fluorescence excited state, which corresponds to

**Table 5**
Spectrophotometrically (UV–Vis) and spectrometrically ($^1$H NMR in parentheses) determined formation constants.

| L | | Zn | Cd | Hg |
|---|---|---|---|---|
| NNN(Qui) | Log $\beta_1$ ML | 5.6 ± 0.1 | 6.1 ± 0.1 | (8.3 ± 0.1) |
| | Log $\beta_2$ $ML_2$ | 10.6 ± 0.1 | 10.8 ± 0.1 | (14.3 ± 0.2) |
| BQAH | Log $\beta_1^*$ ML | 6.1 ± 0.1 | 4.2 ± 0.1 | 8.5 ± 0.1 (8.7 ± 0.1) |
| | Log $\beta_2^*$ $ML_2$ | 11.1 ± 0.1 | 7.5 ± 0.1 | 14.9 ± 0.1 (14.1 ± 0.2) |

[2] It has been noticed that the ligand NNN(Qui) is not fluorescent in water. The formation of the emitting mono-chelate complex $[Zn(NNN(Qui))Cl_2]$ was revealed by its photophysical emission upon addition of $ZnCl_2$ to the free ligand in water (see Ref. [4]).

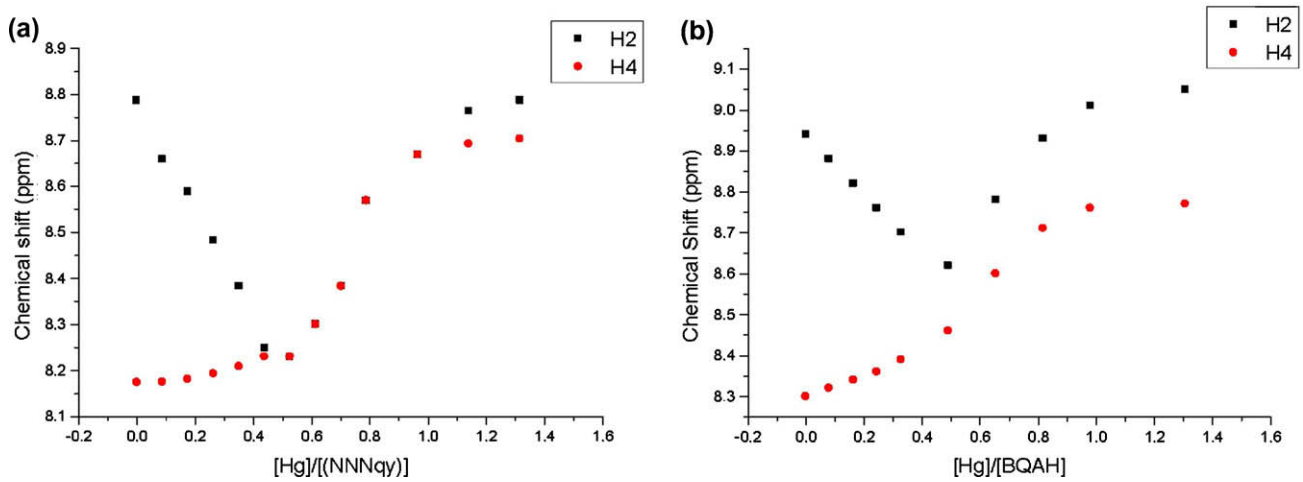



**Fig. 5.** Chemical shift of the $H^2$ and $H^4$ protons of the quinoline moiety of the ligands BQAH (a) and NNN(Qui) (b) as a function of the [Hg]/[L] ratio.

their deprotonated form. A spectroscopic indication for this is the similarity in the energy of the fluorescence maxima for the protonated and deprotonated forms (about 19 000 and 17 000 $cm^{-1}$, respectively).

It is worth mentioning that the irradiation of the complexes $[Zn(BQAH)Cl_2]$ and $[Zn(BQAH)_2](ClO_4)_2$ in $CH_3CN$ at 316 nm excites three different emissions with maxima at 370, 433 and 520 nm, respectively. Similar behavior was observed also in methanol. Apparently, this is related to the dissociation processes which lead to different emitting species $[Zn(BQAH)(CH_3CN)_xCl_y]^{(2-y)+}$ $(0 \leqslant x, y \leqslant 2)$. This assumption is strongly supported by the similarity with the spectral characteristics of authentic samples of independently prepared deprotonated derivatives in different solvents (see Section 2 and Supplementary material).

### 3.5. Determination of the formation constants

#### 3.5.1. Spectrophotometry: general remarks

Owing to the insolubility of the ligand BQAH in water all the equilibrium constants for the related complexes were determined in $CH_3CN$. For the sake of completeness and as an internal check of consistency the formation constants of the complexes of the NNN(Qui) ligand already determined in water [4] were re-determined in acetonitrile. Unfortunately, the spectrophotometric titration of the ligand NNN(Qui) with $Hg(ClO_4)_2$ was unsuccessful owing to the random response of the absorbance data upon $Hg(ClO_4)_2$ addition.

#### 3.5.2. UV–Vis spectrophotometric titrations

Spectrophotometric titration of a $CH_3CN$ solution of the ligands NNN(Qui) or BQAH ([Ligand] $\approx 1 \times 10^{-4}$ mol $dm^{-3}$) with microaliquots of a concentrated solution of the $M(ClO_4)_2$ (M = Zn, Cd, Hg) salt yields the corresponding titration curves which were interpolated by means of the HYPERQUAD 2003 program [7]. In Fig. 4a and b is reported the spectra in the case of the titration of NNN(Qui) and BQAH with $Zn(ClO_4)_2$ in $CH_3CN$.

In any case, the titration curves were resolved on the basis of the following model:

$$M^{2+} + L = ML^{2+} \quad \log \beta_1 \tag{1}$$

$$ML^{2+} + L = ML_2{}^{2+} \quad \log \beta_2 \tag{2}$$

and the ensuing values of the logarithms of equilibrium constants are reported in Table 5.

The acidity of the aminic proton of the ligand BQAH ($pK_a$ = 11.4 in solution of $CH_3CN$:$H_2O$ 1:1 v:v) [6] is somewhat higher than that of the NNN(Qui) moiety which gives no hints of dissociation in water even when coordinated [4]. Such an acidity is increased upon coordination to the cationic center and the deprotonated species $[M(BQA)]^+$ and $[M(BQA)_2]$ form in solution. The concentration of the deprotonated free ligand is however negligible with respect to that of the protonated one almost up to the end of the titration. Thus, taking into account the absorbance changes at 315 nm (at which wavelength the deprotonated $BQA^-$ does not absorb) the determination of the equilibrium constants becomes feasible on the basis of the following model:

$$M^{2+} + BQAH \rightleftharpoons [M(BQAH)]^{2+}{}_{tot} \quad \log \beta_1^* \tag{3}$$

$$[M(BQAH)]^{2+}{}_{tot} + BQAH \rightleftharpoons [(M(BQAH)_2)]^{2+}{}_{tot} \quad \log \beta_2^* \tag{4}$$

$$[BQAH]_0 = [BQAH] + [M(BQAH)]^{2+}{}_{tot} + 2[M(BQAH)_2]^{2+}{}_{tot} \tag{5}$$

where

$$[M(BQAH)]^{2+}{}_{tot} = [M(BQAH)]^{2+} + [M(BQA)]^+ \text{ and}$$
$$[M(BQAH)_2]^{2+}{}_{tot} = [M(BQAH_2)]^{2+} + [M(BQAH)(BQA)]^+ + [M(BQA)_2]$$

Strictly speaking $\beta$ and $\beta^*$ are not directly comparable since the latter represents the product of different constants (i.e. formation and dissociation constants).[3] However, the comparison among the coordinative capability toward zinc and mercury indicates that there are no differences on going from NNN(Qui) to BQAH ligands.

In this respect the most remarkable result emerging from the constants in Table 4 is the increased coordinative discrimination between zinc and cadmium when BQAH is used instead of the ligand NNN(Qui). The increased discrimination could therefore be traced back to the lower acidity of cadmium when compared to zinc or to the enhanced rigidity of the BQAH ligand which significantly disfavors the coordination of the larger $Cd^{2+}$ cation (from Table 5: $\Delta\log \beta_1^*$ = 1.9, $\Delta\log \beta_1$ = − 0.5; $\Delta\log \beta_2^*$ = 3.6, $\Delta\log \beta_2$ = −0.2).

[3] The absorbance of the final complexes is treated as the absorbance of one single species according to the equations:

$$\varepsilon_{MBQAH}{}^*[[M(BQAH)]^{2+}] + \varepsilon_{MBQA}{}^*[[M(BQA)]^+] = \varepsilon_{MBQAHT}{}^*[[M(BQAH)]^{2+}_{tot}]$$

and

$$\varepsilon_{MBQAH2}{}^*[[M(BQAH)_2]^{2+}] + \varepsilon_{MBQAH2\,MBQAH}{}^*[[M(BQAH)(BQA)]^+] + \varepsilon_{MBQA2}{}^*$$
$$\times[[M(BQA)_2]] = \varepsilon_{MBQAH2T}{}^*[[M(BQAH)_2]_{tot}].$$

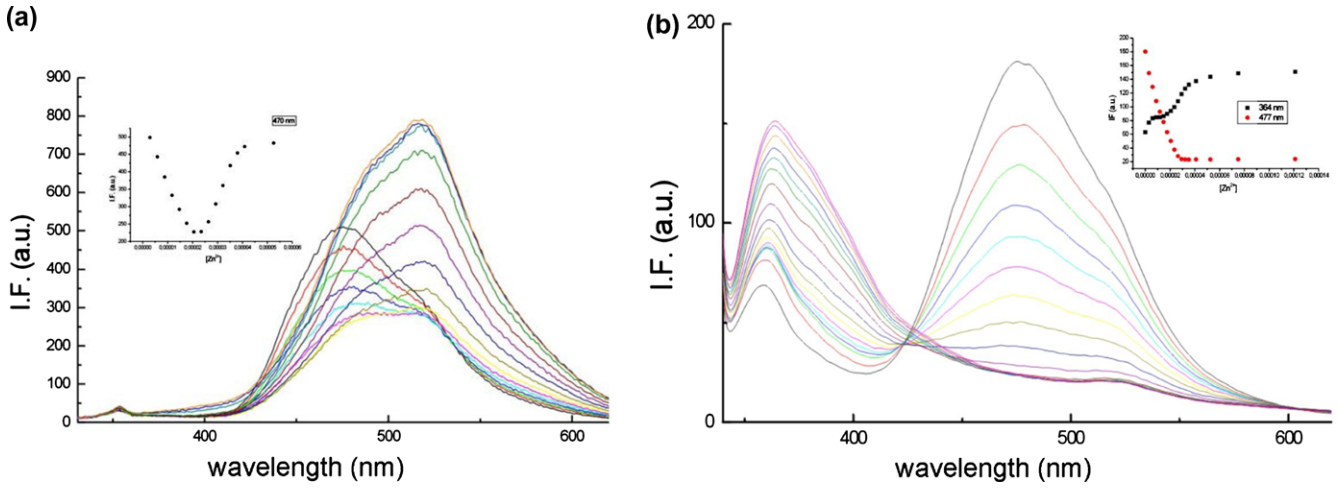



**Fig. 6.** Fluorescence spectra of acetonitrile solutions of NNN(Qui) ($4.3 \times 10^{-5}$ mol dm$^{-3}$; $\lambda_{exc}$ = 321 nm, slit 5/5) (a) and BQAH ($3 \times 10^{-5}$ mol dm$^{-3}$; $\lambda_{exc}$ = 321 nm, slit 5/5), (b) upon addition of $Zn(ClO_4)_2$ (0.005 mol dm$^{-3}$).

Notably, the solvent plays an important role [11]. Thus, on going from water to acetonitrile the formation constants of the cadmium and mercury complexes with NNN(Qui) increases (Cd: from $\beta_1 = 2.99$, $\beta_2 = 6.31$ [4] to $\beta_1 = 6.1$, $\beta_2 = 10.8$; Hg: from $\beta_1 = 5.34$, $\beta_2 = 10.30$ [4] to $\beta_1 = 8.3$, $\beta_2 = 14.3$).

### 3.5.3. $^1H$ NMR spectrometric determination

As can be seen in Table 5 the formation constants for the reaction between the ligand NNN(Qui) and $Hg(ClO_4)_2$ were determined by means of the $^1H$ NMR technique. As a test of internal consistency also the ligand BQAH was titrated with $Hg(ClO_4)_2$ under the same experimental conditions and the ensuing formation constant values are also reported in parentheses in Table 5. The formation constants determined by the two different techniques are reasonably similar and this somehow validates the $\beta$ values determined only by NMR spectrometry. In Fig. 5 the chemical shifts of the $H^2$ and $H^4$ quinoline protons are reported as a function of the Hg/ligand ratio. The trends for both ligands confirm the model proposed before (see the model reported under Fig. 4) and allow the univocal determination of the formation constant although the fast ligand exchange between the complexes and the free ligands induces some broadening of the signals.

### 3.5.4. Spectrofluorimetric validation

The spectrofluorimetric spectra of the solution ensuing from the addition of microaliquots of $M(ClO_4)_2$ (M = Zn, Cd, Hg) to solutions of the ligand NNN(Qui) or BQAH in $CH_3CN$ clearly indicate that the model adopted in the spectrophotometric and spectrometric determination of the formation constants is appropriate.

As can be seen in Fig. 6, fluorescence spectra for the titration of NNN(Qui) and BQAH with $Zn(ClO_4)_2$ display in both cases an isosbestic envelope and such a behavior is somehow confirmed for all the cases studied (see Supplementary material).

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.05.017.

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