An 8-Aminoquinoline-based Fluorescent Sensor of Transition Metal Ions†

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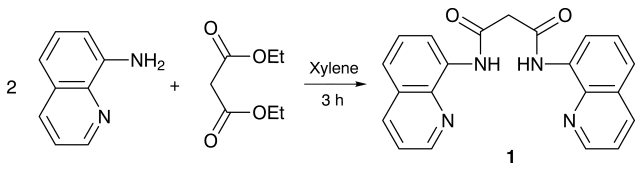
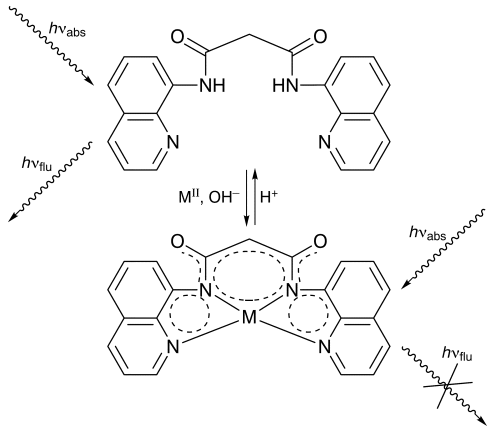
A bis-amide tetradentate ligand, *N,N′*-bis(8-quinolyl)malondiamide (H_2qma) has been prepared and its fluorescent sensitive properties to transition metal ions (Cu^{II}, Co^{II}, Ni^{II} and Mn^{II}) in aqueous DMF are described.

Fluorescence quenching and enhancement have proven useful for the assay of metal ions in solution.[1] Fluorescent sensors for metal ions have been developed by several groups during the past decade.[2] A number of these sensing supramolecules contain anthracene as a fluorescent subunit (or fluorophore). One anthracene-based fluorescence sensor for s block metal ions was developed by de Silva and de Silva[3] and another for d block metal ions by Fabbrizzi *et al.*[4] We have recently been interested in developing a photo-induced electron transfer (PET) sensor for transition metal ions and synthesized a two-component compound **1**, in which a light-emitting group is covalently linked to a receptor specific for metal ions (Scheme 1).



Scheme 1 Synthesis of the fluorescent sensor *N,N′*-bis(8-quinolyl)malondiamide (H_2qma)

Compound **1** displays the typical emission spectrum of 8-aminoquinoline in dimethylformamide (DMF)–water (4:1, v/v) solution, and its fluorescence intensity does not vary over the pH range 2–12. The amide protonation state of the dioxotetraaza unit does not alter the fluorescence of the adjacent quinolyl unit. However, if 1 mol equivalent of Ni^{II} is added to an acidic solution of **1**, the fluorescence intensity I_f steadily decreases upon titration with NaOH. Complete fluorescence quenching is observed when the excess of strong acid has been neutralized and 2 further equivalents of OH^- have been added.



Scheme 2

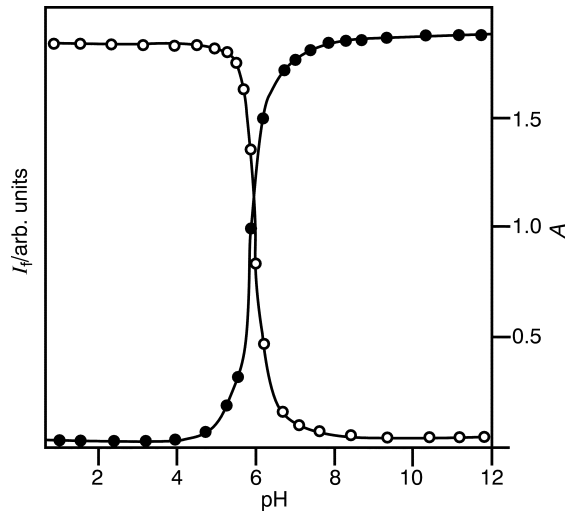


Fig. 1 Dependence of the fluorescence intensity (I_f, ○) on pH and the absorbance (A) of the band at 420 nm (●) for a solution of equimolar amounts of **1** and Ni^{II} in DMF–water (4:1, v/v)

The plot of I_f *vs.* pH (Fig. 1) displays a sigmoidal curve typical of a switching effect. An analogous titration experiment was performed inside a spectrophotometric cuvette in order to study the quenching mechanism. When NaOH was added, the solution becomes brown, and an absorption band at 420 nm develops. The absorbance A reaches its limiting value after two amide-H atoms were neutralized. The pH-spectrophotometric profile (Fig. 1) shows a sigmoidal curve, which is symmetrical to the pH–fluorescence profile and centered at pH ≈ 6. Deprotonation of the two amide groups yields a tetradentate N_4 ligand L^{2-},

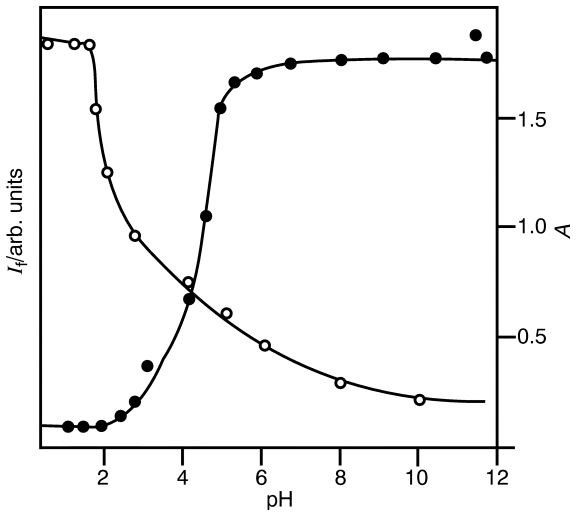


Fig. 2 Dependence of the fluorescence intensity (I_f, ○) on pH and absorbance (A) of the band at 420 nm (●) for a solution of equimolar amounts of **1** and Cu^{II} in DMF–water (4:1, v/v)

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

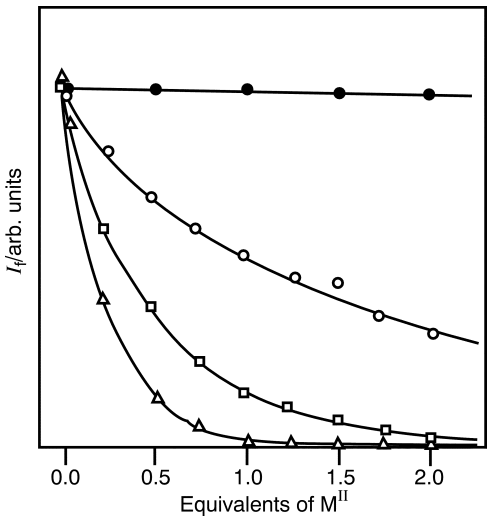

Fig. 3 Fluorescence intensity of a solution of **1** (10 μM) upon titration with Mn^{II} (●), Cu^{II} (○), Co^{II} (□) or Ni^{II} (▲) in a solution of DMF–water (4:1, v/v)

which chelates d block metal ions, leading to a square-planar quasi-aromatic metal complex (Scheme 2).

This demonstrates that the fluorescence quenching of **1** is associated with the coordination of Ni^{II} by the dioxotetraaza unit of **1**. The fluorescence quenching is induced from Ni^{II}-to-quinolyl electron transfer. When 1 mol equivalent of Cu^{II} is added to a solution of **1** in aqueous DMF, the pH–fluorescence profile and the pH–spectrophotometric absorbance profile yield two symmetrical sigmoidal curves but these are not centered at the same pH (Fig. 2).

The coordination ability of Cu^{II} to **1** is stronger than Ni^{II}. Before deprotonation of the two amide groups an electron transfer from d orbitals of Cu^{II} to the excited π orbital of quinolyl of **1** has already occurred. Fluorescence quenching begins at pH = 2 and ends after neutralization of the excess strong acid and after addition of 2 further equivalents of base. By contrast, when 1 mol equivalent of Mn^{II} is added to a solution of **1** in DMF–water (4:1, v/v), the fluorescence intensity does not change over the pH range 2–12. The absence of fluorescence quenching by Mn^{II} can be explained by the fact that the ion is coordinated only very weakly with the dioxotetraaza unit of **1**, and that deprotonation of the two amide groups is endothermic.

Fluorescence of compound **1** can be observed by titration with quenching metal ions (such as Cu^{II}, Co^{II}, *i.e.* open-shell, paramagnetic, large or easily reducible cations) as shown in Figs. 3 and 4. Experiments were carried out at concentrations of 10 μM in DMF–water (4:1, v/v). We have observed that the sequence of quenching ability is $Ni^{II} > Co^{II} > Cu^{II}$. At the same time the fluorescence titration experiment also confirms that Mn^{II} is not coordinated by the dioxotetraaza unit of **1** since fluorescence quenching is not observed even in strongly basic solution. The Mn^{II} ion does not profit from ligand field effects and thus neither promotes deprotonation of the amide group nor is chelated by the dioxotetraaza unit of **1**. Additionally Mn^{II} in aqueous DMF is not redox active and does not possess any empty low-energy orbitals, which are essential for energy transfer and radiationless decay of the quinolyl excited state.

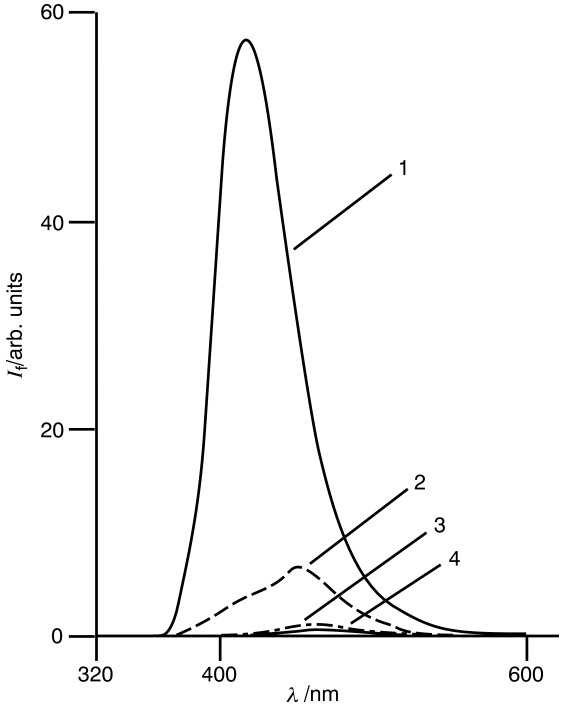

Fig. 4 Fluorescence intensity of a solution of **1** (10 μM) upon titration with Ni^{II}: (1) 0, (2) 0.5, (3) 1 and (4) 1.5 equivalents

Experimental

IR spectra were recorded as KBr pellets on a Shimadzu IR-470 spectrometer. ^{1}H NMR spectra were obtained on a JEOL FX90Q F-T instrument. Elemental analyses for C, H and N were determined using a Perkin-Elmer 240C analyser based on the classical Pregl Dumas method. Mp was taken on an electrothermal melting point apparatus and was uncorrected. Mass spectrum was obtained by use of VG ZAB-HS mass spectrometer. Fluorescence measurements were made on a Hitach 850F luminescence spectrometer. Absorbances (*A*) were obtained on a Shanghai 721 spectrophotometer.

N,N′-bis(8-*quinolyl*)*malondiamide* **1**[5].—8-Aminoquinoline (14.4 g, 0.1 mol) and diethyl malonate (8.0 g, 0.05 mol) were added to 200 ml xylene. The solution was heated at reflux for 3 h under an N_2 atmosphere and the product recrystallized from acetone. Yield 81.0%; mp 218.5–219.5 °C; IR (KBr, neat) 3290, 1650, 1530, 1480, 1420, 1375, 1320 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.874 (s, 2 H), 7.255–7.641 (m, 6 H), 8.082–8.906 (m, 6 H), 10.770 (s, 2 H); MS *m/z* for $C_{21}H_{16}N_4O_2$ 356(M^+). Anal. Calc. C, 70.77; H, 4.53; N, 15.72. Found: C, 70.42; H, 4.66; N, 15.60%.

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