8-Hydroxyquinoline Based Multipodal Systems: Effect of Spatial Placement of 8-Hydroxyquinoline on Metal Ion Recognition

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Abstract

The complexation behaviors of tetrapod 1,2,4,5-tetrakis(8-hydroxyquinolinoxymethyl) benzene (**1**) and dipod 1,2-bis(8-hydroxyquinolinoxymethyl)benzene (**2**) have been determined by fluorescence spectroscopy in $CH_3CN−H_2O$ (4:1) buffered at pH 6.9 [HEPES 10 mM] and by ^1H NMR in CD_3CN-$CDCl_3$ (1:1) mixture. Tetrapod **1** can recognize Ag^+ (10−40 μM) even in the presence of (500 μM) of alkali and alkaline earth metal ions. However, transition metal ions interfere in the estimation of Ag^+. Dipod **2** shows poor selectivity towards Ag^+. The ^1H NMR based titrations of podands **1** and **2** against $AgNO_3$ show characterstic changes in chemical shifts in quinoline, methylene and aromatic protons. The spectral fitting of fluorescence and ^1H NMR titration data has been used to evaluate the stoichiometries of complexes and their complexation constants.

Introduction

The design and synthesis of target selective receptors with luminescent signaling systems for direct measurement of changes in emission intensities or wavelength, arising due to perturbation upon ion or molecular recognition, have attained a central position in supramolecular chemistry [1−2].

These recognition phenomena depend primarily on multiple host-guest interactions. Locking of conformations of both the host and the guest makes negative contributions to total free energies of the system [3]. So, in addition to the complementary of binding sites, the correct spatial placement of subunits [4] constitutes a major criterion for designing new receptors.

In the case of planar platforms, the contribution of molecular architectures arising due to placement of two or three subunits at 1,3- or 1,3,5-positions on a benzene ring has been well studied in molecular recognition [5]. However, the supramolecular behavior of receptors possessing two or four such functional groups placed symmetrically at 1,2- and 1,2,4,5-positions of a benzene ring has been scarcely studied [6].

8-Hydroxyquinoline (Oxine) and its derivatives are known to be the best chelaters after EDTA and its derivatives due to their guest modulated chromogenic and fluorescent behavior. Accordingly, they have attained prime significance and have been used in chromatography [7], detection of metal ions [8], in organic light emitting diode devices [9], and in electrochemiluminescence [10] etc.. 8-Hydroxyquinoline, due to

proton transfer between OH and Py-N functions, is weakly fluorescent but its O-alkyl derivatives due to lack of this phenomenon exhibit high fluorescence [11]. Therefore, many receptors having O-alkylated 8-hydroxyquinoline have been reported [12−14].

Earlier, we have reported that 8-alkoxyquinoline based tripod showed selective quenching with Cu^{2+} and could be used for the estimation of Cu^{2+} even in the presence of elevated concentrations of interfering metal ions [14]. Now we report that tetrapod **1**, possessing four quinoline units at 1,2,4,5 positions of benzene ring, in $CH_3CN−H_2O$ (4:1) buffered at pH 6.9 [HEPES 10 mM], can be used for estimation of 1−40 μM Ag^+ even in the presence of 500 μM alkali and alkaline earth metal ions. Dipod **2** shows poor selectivity towards Ag^+. The characteristic changes in chemical shifts in ^1H NMR signals of **1** and **2** on addition of $AgNO_3$ and lack of these changes in case of 8-methoxyquinoline point to the role of spatial placement of quinoline moieties on the benzene ring.

Experimental

Tetrapod 1,2,4,5-tetrakis(8-hydroxyquinolinoxymethyl)benzene (**1**), dipod 1,2-bis(8-hydroxy quinolinoxymethyl) benzene (**2**) and 8-methoxyquinoline (**3**) were synthesized as reported in literature [15, 16].

Extraction of metal picrates

For the extraction experiments, metal picrate solutions (0.001 mol dm^{-3}) were prepared in deionized distilled

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water. The solutions of receptors (0.001 mol dm^{-3}) were prepared in chloroform (A.R Grade). An aqueous solution (2 mL) of a metal picrate (0.001 mol dm^{-3}) and a chloroform solution (2 mL) of a receptor (0.001 mol dm^{-3}) in a cylindrical tube closed with a septum was shaken for 5 min and kept at 27 ± 1 °C for 3−4 h. An aliquot of the chloroform layer (1 mL) was withdrawn with a syringe and diluted with acetonitrile to 10 mL. The UV absorption was measured against CHCl$_3$−CH$_3$CN (1:9) solution at 374 nm. Extraction of the metal picrate has been calculated as the percentage of the metal picrate extracted in the chloroform layer and values are the mean of the three independent measurements which were within ± 0.02 error.

UV-Vis and fluorescence experiments

UV-Vis absorption and fluorescence spectra were recorded on Shimadazu UV-1601-PC spectrophotometer and Shimadazu RF1501 spectrofluorophotometer with a 1 cm quartz cell at 25 ± 0.1 °C. The solutions of **1−3** in double distilled acetonitrile and metal nitrates were prepared in double distilled water. The number of solutions containing **1−3** (1 μM) and different concentrations of metal nitrates were prepared and were kept at 25 ± 1 °C for 2 h before recording their absorption or fluorescence spectra. The spectra obtained were analyzed through curve fitting procedures by using SPEC-FIT 3.0.36 to determine the stability constants and the distribution of various species.

NMR titrations

The complexation behaviors of podands **1−3** towards Ag$^+$ have been investigated by titration of solution of a receptor against AgNO$_3$. Due to poor solubility of **1** in CD$_3$CN, all the titrations have been performed in CD$_3$CN−CDCl$_3$ (1:1 v/v) mixture. The ^{1}H NMR measurements were carried out at 25 ± 0.1 °C probe temperature. The solutions of podands **1−3** (0.001 mol dm^{-3}) were titrated by gradual addition of 0.01 ml of AgNO$_3$ (0.01 mol dm^{-3}) and each time the ^{1}H NMR spectrum was recorded.

Results and discussion

Extraction behavior

The binding behaviors of **1** and **2** were determined through receptor mediated extraction of metal picrates in CHCl$_3$-water system. In the liquid−liquid extraction experiments of **1** towards various metal ions, tetrapod **1** (10^{-3} M) extracted Ag$^+$ 83% where as alkali and alkaline earth metal ions were extracted up to 1−2 % only. Dipod **2** extracted silver nearly 79% where as alkali and alkaline earth metal ions were extracted in < 3 % amounts. These extraction results show the preferential extraction of Ag$^+$ amongst alkali, alkaline earth and Tl$^+$ picrates (Table 1).
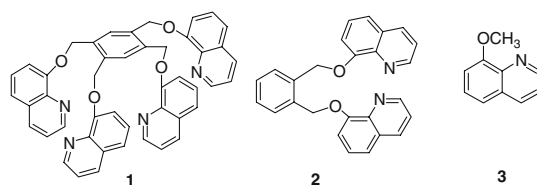

Table 1. Extraction (%) profiles of tetrapod 1 and dipod 2

Metal ion	Extraction (%)	
	Tetrapod **1**	Dipod **2**
Li$^+$	0.27	1.18
Na$^+$	0.32	1.06
K$^+$	0.42	1.15
Tl$^+$	2.23	2.03
Ag$^+$	83.15	78.00
Mg^{2+}	0.34	0.79
Ca^{2+}	0.50	0.96
Sr^{2+}	0.42	0.88
Ba^{2+}	0.54	1.04

Photophysical behavior of podands 1−3 towards transition metal ions

Podands **1** and **2** (10 μM, CH$_3$CN−H$_2$O, 4:1) in their UV-visible spectra display broad absorption bands at λ_{max} 305 nm due to the 8-alkoxyquinoline moiety. The solutions of podands **1** and **2** on excitation at λ_{max} 305 nm exhibit fluorescence spectra − typical of the 8-alkoxyquinoline moiety with λ_{max} at 400 nm, and remain stable within λ_{ex} 304 to 360 nm. In the concentration range 1−40 μM, the fluorescence of **1** and **2** is directly proportional to their concentration. This linear increase in fluorescence with concentration indicates that podands **1−3** are not susceptible to self quenching and to aggregation processes in this concentration range.
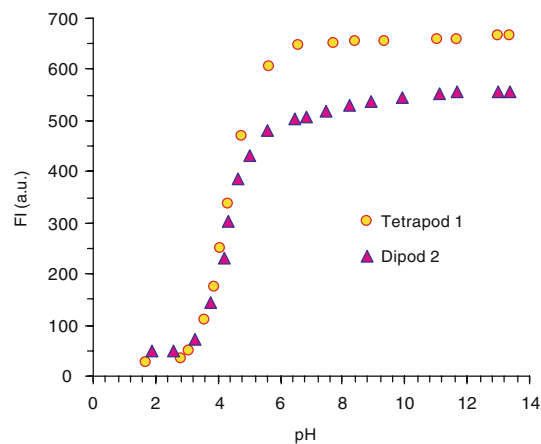

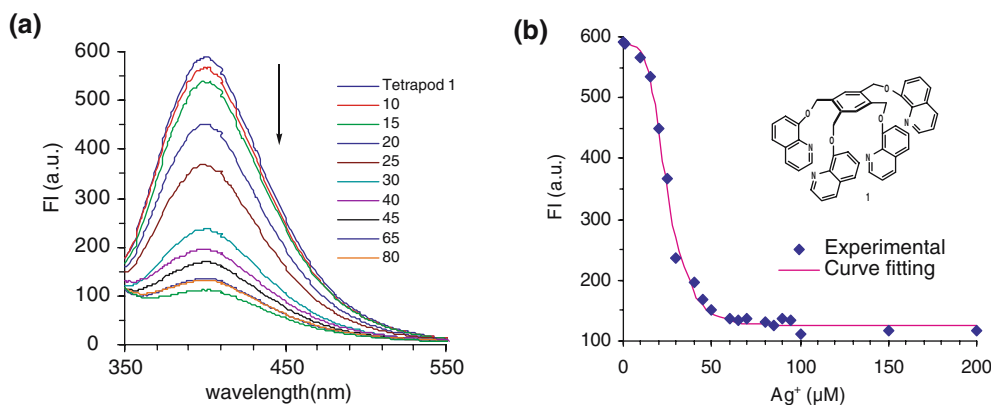*Figure 1.* The effect of pH on the fluorescence intensity of tetrapod **1** and dipod **2** (1 μM, CH$_3$CN−H$_2$O; 4:1).

Figure 2. (a) The effect of Ag$^+$ on the fluorescence spectrum of tetrapod **1** and (b) Curve fitting of change in FI of tetrapod **1** at 400 nm on addition of AgNO$_3$. (■) experimental points, (--) fitted line.

The tetrapod **1** possesses four quinoline nitrogens and would undergo protonation in the presence of acid. The titrations of **1** (1 μM, CH$_3$CN–H$_2$O; 4:1) with acid and base showed that fluorescence intensity between pH 14–6.5 remained unaffected and lowering the pH from 6.5 to 3.0 resulted in sharp decrease (∼90%) in the fluorescence intensity. Further lowering of pH below 3.0 did not affect the fluorescence intensity and plateau was achieved (Figure 1). During this pH titration the sequential protonation of four quinoline moieties has been not observed. Probably the sequential protonation has a very small difference in pKa and an average pKa of 4.37 ± 0.05 is observed.

Similarly the dipod **2** showed fluorescence quenching between pH 6.5–3.0 and curve fitting of the data shows pKa of 4.3 ± 0.05. Therefore, protonation of quinoline nitrogens between pH 6.5–3.0 results in fluorescence quenching and beyond pH 6.5, free quinoline moieties are available for complexation. As a result, the effect of metal ions on the fluorescence behavior of **1** and **2** has been determined at pH ∼6.9 (HEPES buffer, 10 mM).

In the preliminary fluorescence studies, tetrapod **1** (1 μM) at pH 6.9 (HEPES 10 mM) in CH$_3$CN–H$_2$O (4:1) in the presence of 100 μM concentration of Ag$^+$, Cu^{2+} and Hg^{2+} showed significant fluorescence quenching with Ag$^+$ (∼80%), Cu^{2+} (∼60%), and Hg^{2+} (∼70%) whereas addition of 100 μM Ni^{2+}, Zn^{2+}, Cd^{2+} and Co^{2+} quenched emission of **1** by 5–15% only. The addition of alkali or alkaline earth metal ions (100 μM) did not affect the fluorescence of **1**. Therefore, **1** shows selective fluorescence quenching with Ag$^+$, Hg^{2+} and Cu^{2+} only and may be used for their quantitative estimation.

A solution of tetrapod **1** [1 μM, CH$_3$CN–H$_2$O (4:1), HEPES buffer (10 mM), pH 6.9] on the addition of AgNO$_3$ showed fluorescence quenching, which gradually increased with increasing concentration of AgNO$_3$. The plot of fluorescence intensity of **1** at 400 nm vs. concentration of AgNO$_3$ exhibits gradual decrease in fluorescence intensity with the increase in the concentration of AgNO$_3$ between 1 and 40 μM, after which the fluorescence levels off and plateau is achieved (Figure 2). Thus tetrapod **1** can estimate 10–40 μM conc. of Ag$^+$ through fluorescence spectroscopy.

The spectral fitting of the data shows that at < 10 μM AgNO$_3$ small amounts of ML$_2$ complex (log β_{ML2} = 9.9 ± 0.4) is formed but on further addition of AgNO$_3$, the formation of only M$_4$L complex (log β_{M4L} = 18.7 ± 0.2) is observed (Figure 3).

Although except Ag$^+$, Cu^{2+} and Hg^{2+}, the presence of other metal ions studied did not affect the fluorescence of **1** individually, in order to explore the utility of **1** as a Ag$^+$ selective fluoroionophore, the titration of **1** with Ag$^+$ in the presence of probable interfering metal ions Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Cu^{2+}, alkali and alkaline earth metal ions was performed.

The plot of fluorescence of **1**-Ag$^+$ and **1**-Ag$^+$-M^{Z+} solutions with respect to concentration of Ag$^+$ shows that the fluorescence intensity as observed in the case of the **1**-Ag$^+$ complex does not vary in the presence of 500 μM of Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} cations. Cs$^+$ and Li$^+$ when present in relatively lower concentration (100 μM) do not interfere in estimation of Ag$^+$. The poor extraction of alkali and alkaline earth metal picrates (Table 1) by tetrapod **1** shows poor binding of these metal ions with tetrapod **1**. So, lack of interference of these metal ions in estimation of Ag$^+$ could be attributed by and large to their poor binding. The change in photophysics of **1** with alkali and alkaline

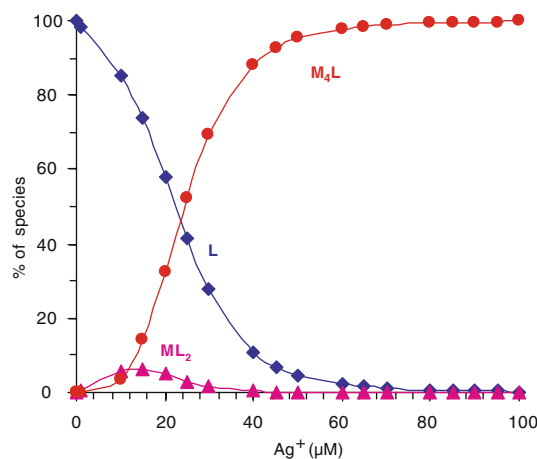*Figure 3.* The percent formation of ML$_2$ and M$_4$L species of tetrapod **1** (1 μM, CH$_3$CN–H$_2$O (4:1), pH 6.9) on addition of AgNO$_3$ (100 μM).

(a)

(b)

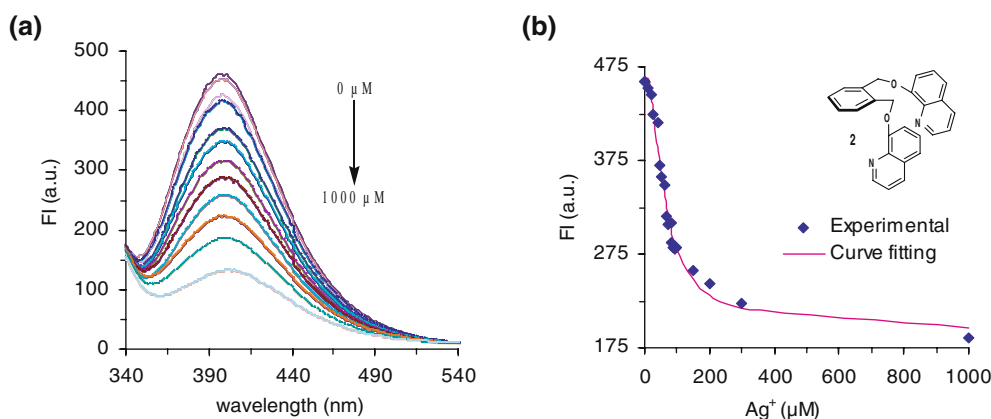*Figure 4.* (a) The effect of Ag^+ on the fluorescence spectrum of dipod **2** and (b) Curve fitting of change in FI of dipod **2** (1 μM) at 400 nm on addition of $Ag(NO_3)$. (■) experimental points, (--) fitted line.

earth metal ions, if at all, has only small contribution. Therefore, **1** can estimate $10-40$ μM of Ag^+ through fluorescence spectroscopy even in the presence of alkali and alkaline earth metal ions. The presence of transition metal ions causes enhanced quenching of **1** as observed with only Ag^+ and can not be used in estimation of Ag^+ in the presence of transition metal ions.

The solution of dipod **2** [1 μM, $CH_3CN:H_2O$ (4:1)] pH 6.9 on addition of 100 μM concentration of metal ions showed fluorescence quenching with Ag^+ (50%), fluorescence enhancement with Cd^{2+} (55%) whereas Cu^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Co^{2+} did not affect the fluorescence of **2**.

The plot of fluorescence intensity of **2** against concentration of Ag^+ shows gradual decrease in fluorescence up to 200 μM of Ag^+ and then trails to a residual value up to 1000 μM Ag^+. The spectral fitting of the data shows the formation of ML (log β_{ML} = 3.86 ± 0.25) and M_2L (log β_{M2L} = 8.74 ± 0.10) complexes (Figure 4b). Therefore dipod **2** shows significantly lower sensitivity to $AgNO_3$ than tetrapod **1**.

8-Methoxyquinoline **3** [1 μM, CH_3CN-H_2O (4:1), HEPES buffer (10 mM), pH 6.9] on addition of excess of transition metal ions showed the non-selective quenching and points to the organization of four quinoline moieties in **1** for selective Ag^+ encapsulation. Similar role of organization of four quinoline units in **1** further supported by NMR titration results discussed in proceeding section.

In contrast to Cu^{2+} selectivity in case of tripod possessing three quinoline moieties at 1,3,5 position, the placement of four quinoline units on benzene platform at 1,2,4,5 positions in tetrapod **1** leads to preference for Ag^+ though with lower selectivities. Therefore, the spatial placement of quinoline moieties on benzene ring significantly affects their photophysical behavior towards metal ions.

¹H NMR Titration Studies of podands 1 and 2

The complexation behavior of podands **1** and **2** towards Ag^+ has been investigated by titration of solution of a receptor against $AgNO_3$. Due to poor solubility of **1** in

CD_3CN, all the titrations have been performed in $CD_3CN-CDCl_3$ (1:1 v/v) mixture. Since, some of the signals overlap with each other, the change in chemical shift of only benzene H, HQH-4, HQH-2, HQH-7, CH_3 and OCH_2 signals have been recorded.

The titration of tetrapod **1** with $AgNO_3$ showed gradual downfield shift of benzene H and hydroxyquinoline H-4 (HQ H-4) protons with increase in the concentration of $AgNO_3$ up to 1 equivalent and then plateau was achieved.

The proton signals due to OCH_2 and HQ H-2 protons underwent upfield shift up to addition of 0.5 equiv. of $AgNO_3$. On further addition of $AgNO_3$, the signals move downfield till 1 equiv. of $AgNO_3$ and then plateau was achieved (Figure 5). This reversal in chemical shift of proton signals [17] on addition of $AgNO_3$ points to the presence of more than one stoichiometric complexes between **1** and $AgNO_3$. The curve fitting of the data shows that up to 0.5 equiv. $AgNO_3$ addition mainly ML_2 − a sandwich type complex is formed and on further increasing concentration of $AgNO_3$, the contribution of ML_2 gradually decreases and that of ML and M_4L species increases. At 2 equiv. of $AgNO_3$ ML_2, ML
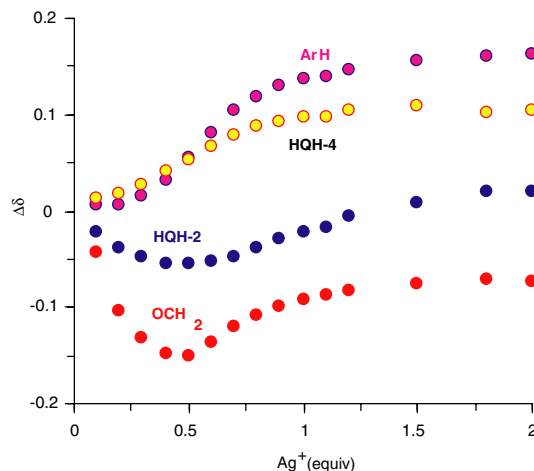

Figure 5. ¹H NMR spectral changes (300 MHz, $CD_3CN-CDCl_3$) for tetrapod **1** (10^{-3} M) upon addition of $AgNO_3$. (●) OCH_2 (■) HQH-2 (●) HQH-4 and (◆) ArH. The positive values denote downfield and negative values upfield chemical shifts.

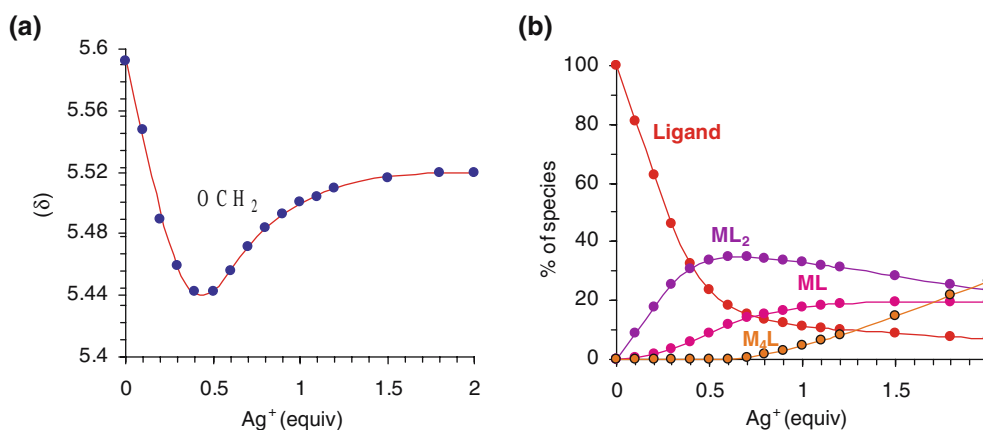**Figure 6.** (a) The curve fitting of ^1H chemical shift value of OCH$_2$ protons of tetrapod **1** (10^{-3} M) (■) experimental points (--) fitted line (b) % formation of ML, ML$_2$ and M$_4$L species with the gradual addition of AgNO$_3$.
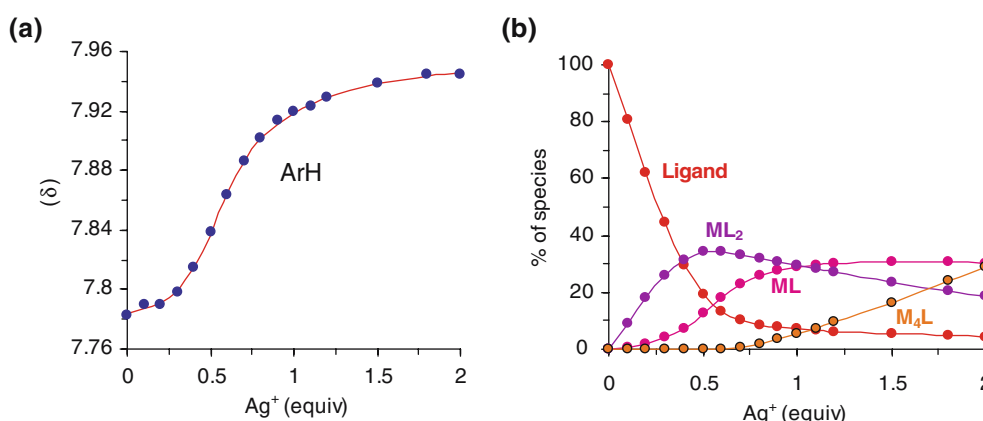

Figure 7. (a) The curve fitting of ^1H chemical shift value of ArH protons of tetrapod **1** (10^{-3} M) (■) experimental points (--) fitted line (b) % formation of ML, ML$_2$ and M$_4$L species with the gradual addition of AgNO$_3$.

and M$_4$L are present in $\sim$24%, 25% and 22% amounts respectively and exhibit stability constants log β_{ML2} = 8.5 ± 0.4; log β_{ML} = 4.1 ± 0.4 and log β_{M4L} = 13.9 ± 0.8 (Figures 6, 7).

The ^1H NMR tirations of **1** have been performed at 1 mM concentration i.e. nearly 1000 times more than the

Figure 8. ^1H NMR spectral changes (300 MHz, CD$_3$CN–CDCl$_3$) for dipod **2** (10^{-3} M) upon addition of AgNO$_3$. (▲) OCH$_2$ (●) HQH-2 (◆) O-Xylene (●) HQH-4 (■) HQH-7. The positive values denote downfield and negative values upfield chemical shifts.

concentration (1 μM) at which fluorescence studies have been performed. The difference in species distribution observed under two experimental conditions may be attributed to this large difference in concentration of **1**.

The dipod **2** on ^1H NMR titration with AgNO$_3$ showed that OCH$_2$ and HQH-2 protons shifted upfield and HQH-4 and HQH-7 protons shifted downfield (Figure 8). All the protons titration curves show plateau near 0.5 equiv. of AgNO$_3$ and indicate the formation of only ML$_2$ complex (log β_{ML2} = 9.2 ± 0.4) (Figure 9). The negligible changes in chemical shifts in ^1H NMR of podand **3** on titration with AgNO$_3$ show lack of complexation of **3** with AgNO$_3$.

Therefore, though 8-methoxyquinoline does not complex with Ag$^+$, the placement of two and four quinoline moieties on benzene platform in dipod **2** and tetrapod **1** leads to increased complexation and number of stoichiometric complexes.
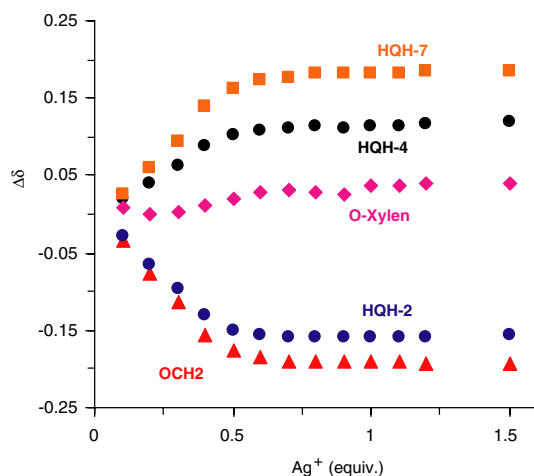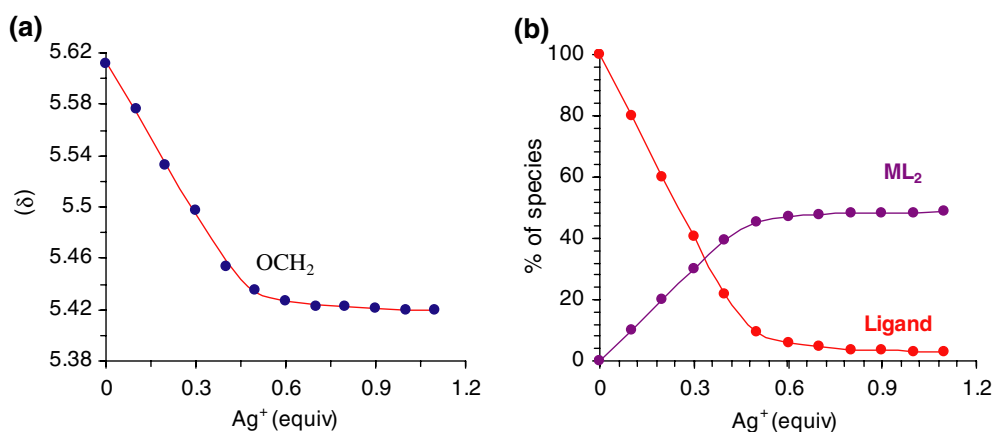
Acknowledgments

Figure 9. (a) The curve fitting of ^1H chemical shift value of OCH$_2$ protons of dipod **2** (10^{-3} M) (■) experimental points (--) fitted line. (b) % formation of ML$_2$ species with the gradual addition of AgNO$_3$.

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