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Photoactive Chemosensors 2: 8-Hydroxyquinoline Based Cu(II) Selective Fluorescent Tripod

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Photoactive Chemosensors 2: 8-Hydroxyquinoline Based Cu(II) Selective Fluorescent Tripod

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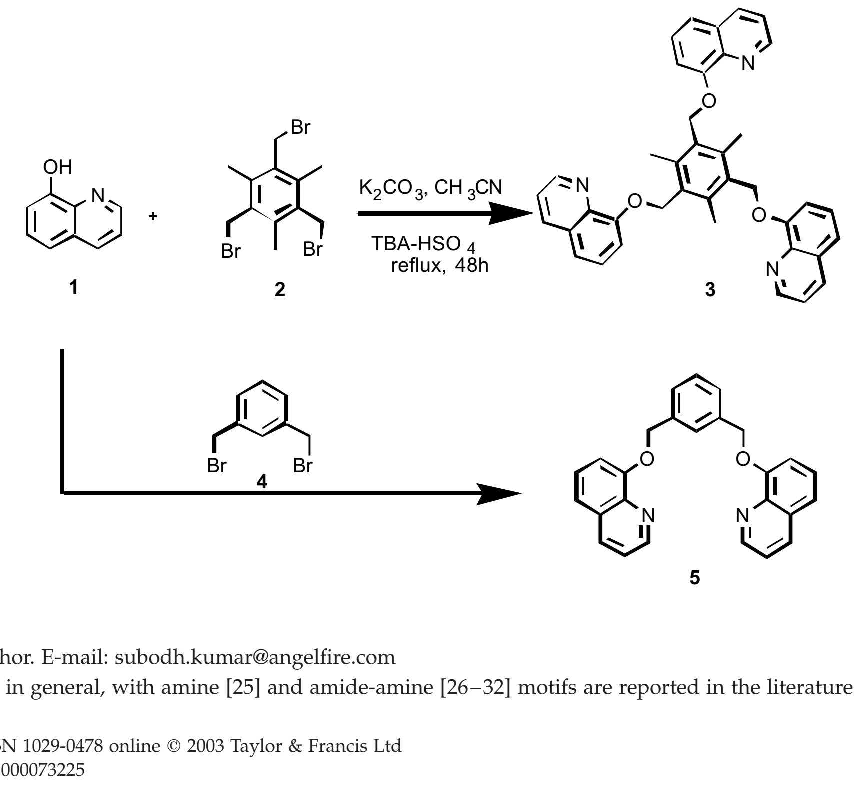
8-Hydroxyquinoline based tripod 3 shows selective fluorescence quenching with Cu(II) and can be used for estimation of Cu(II) (1–6 ppm) even in the presence of Ni(II), Cd(II), Zn(II) (1000 ppm), Ag(II) (100 ppm).

Keywords: Proactive chemosensors; 8-Hydroxyquinoline; Fluorescent tripod; Podand

The distinct advantage of fluorescent receptors in terms of sensitivity, selectivity and response time over conventional receptors has encouraged the design and synthesis of a large number of fluorescent ionophores [1–3]. In photoinduced electron transfer cation sensors naphthalene [4–6], anthracene [7–10], pyrene [11–14] have, in general, been used as fluorescent moieties. Historically the bidentate metal binding ability of pyridine N and deprotonizable OH in 8-hydroxyquinoline and its derivatives has been used for fluorometric determination of Zn(II), Al(II), Mg(II) and several other cations [15,16] with varied interferences. More recently, 8-hydroxyquinoline appendage in lariat ethers has been used for developing K(I) [18,19], Mg(II) [20], Cd(II) [21], Hg(II) [22] and Zn(II) [23,24] selective fluorescent sensors. Except for the Li(I) [17] selective podand, all these 8-hydroxyquinoline based chemosensors require additional ether, thioether and/or amine binding sites for complexation with metal ions. Here, we report Cu(II) selective tripod **3** which possesses 8-hydroxyquinoline moieties as only binding units.[†]



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[†] The Cu(II) sensors, in general, with amine [25] and amide-amine [26–32] motifs are reported in the literature.

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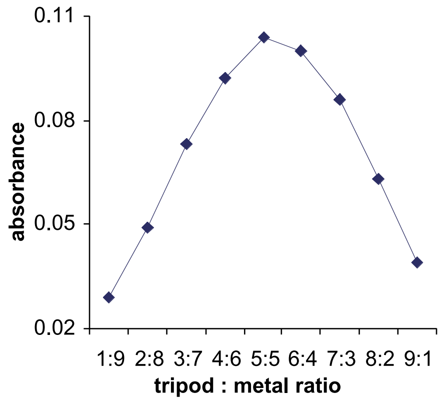

FIGURE 1 Job plot for stoichiometric determination.

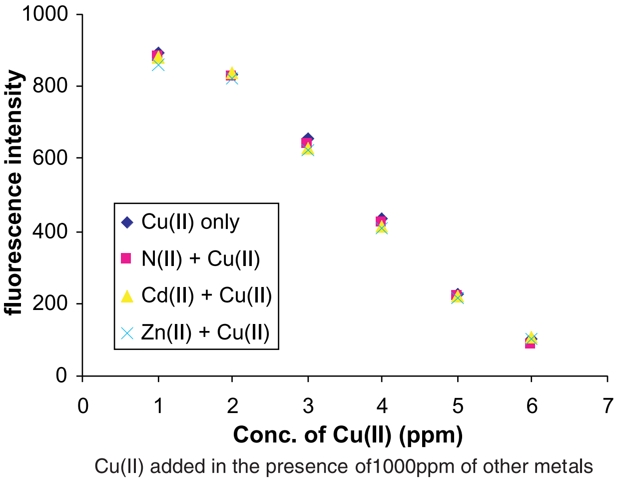

FIGURE 2 Change in fluorescence intensity on addition of metal salts.

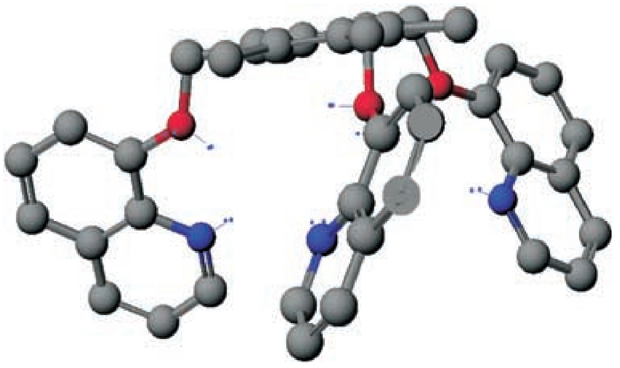

FIGURE 3 The energy minimized structure of tripod **3**.

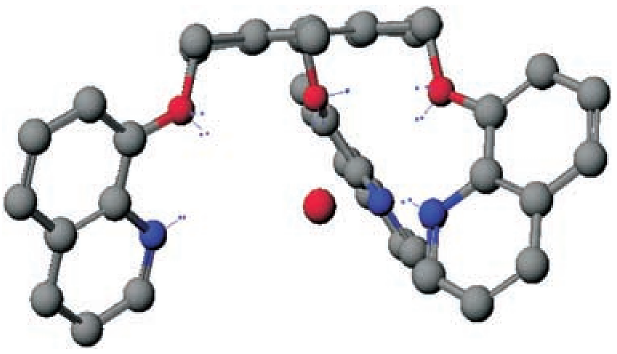

FIGURE 4 The energy minimized structure of **3**-Cu(II) complex.

It shows >90% quenching with Cu(II) (6 ppm) and can estimate Cu(II) even in the presence of elevated levels of Ni(II), Cd(II), Zn(II) (1000 ppm) and Ag(I) (100 ppm).

The tripod **3**[‡] in its absorption spectrum shows λ_{max} at 304 nm in CH_3CN:H_2O (4:1). **3** on excitation at 305 nm shows emission at 398 nm. At 10^{-7} M of **3**, the addition of 10 ppm of Cu(II) causes total quenching of fluorescence while other metal ions (10 ppm) (Ni(II), Cd(II), Zn(II), Ag(I), Pb(II) and Hg(II)) do not affect the emission spectrum of **3**. Podand **5** at 10^{-6} M shows fluorescence quenching on addition of Cu(II) (10–50 ppm) and then attains a plateau.

Tripod **3** (50 ppm) in CH_3CN:H_2O (4:1) shows λ_{max} at 304 nm. On incremental addition of copper nitrate (5–50 ppm), an increase in absorption in 355–410 nm region is observed, which attains a plateau at 50 ppm of Cu(II). This is also accompanied by a gradual shift of λ_{max} from 304 to 316 nm. The Job plot of **3** with copper nitrate shows 1:1 complexation (Fig. 1).

The titration of **3** (0.1 ppm) with Cu(II) causes gradual fluorescence quenching from 1–6 ppm concentration and then a plateau is achieved. In order to further explore the utility of **3** as Cu(II) selective fluorescent chemosensor, the titration of **3** with Cu(II) in the presence of excess of other metal ions has been performed. The presence of Ni(II), Cd(II) and Zn(II) (1000 ppm) and of Ag(I) (100 ppm) does not interfere in the estimation of 1–6 ppm of Cu(II) (Fig. 2). Cu(II) can be estimated even in the presence of Hg(II), if present in 10 ppm in concentration.

In case of podand **5** [33], the poor sensitivity towards Cu(II) (90% quenching by 50 ppm Cu(II)) and high order of interference by Ag(I) and Ni(II) emphasize the role of organization of the three 8-hydroxyquinoline moieties in tripod **3** towards Cu(II) selectivity.

The energy minimization of tripod **3** (Fig. 3) and its complex (Fig. 4) have been performed by using CAChe work system 3.11 software.[¶] The energy

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[‡] **3** (34%), m.p. 200–202°C; CI *m/z* 592[M + H]$^+$; ^{1}H NMR ($CDCl_3$): δ 2.51 (9H, s, 3 × CH_3), 5.33 (6H, s, 3 × CH_2), 7.21 (3H, dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 3 × HQ-H3), 7.32–7.49 (9H, m, 3 × HQ-H5, 6, 7), 8.08 (3H, dd, $J_1 = 10$ Hz, $J_2 = 4$ Hz, 3 × HQ-H4), 8.88 (3H, dd, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 3 × HQ-H2); ^{13}C NMR (normal) ($CDCl_3$): δ 116.38, 66.72, 109.96, 120.05, 121.59, 126.73, 129.56, 131.48, 135.69, 140.04, 140.67, 149.29, 155.20; $C_{39}H_{33}N_3O_3$ requires (%) C = 79.19, H = 5.58, N = 7.12 found C = 79.2, H = 5.6, N = 7.1%.

[¶] The energy minimization studies have been performed with CAChe work system 3.11 by using MM3 calculations. The hydrogens have been omitted only from the final view.

minimization of **3** shows it to have different conformations i.e. planar (66 kcal/mol) to tripodal (54 kcal/mol). The steric repulsions between CH_3 and ether –O– in the planar conformation lead to a more stable tripodal conformation. Compound **3** seems to be preorganized for metal complexation and on addition of Cu(II) undergoes further stabilization to 42 kcal/mol.

Further studies on tripods and podands based on 8-hydroxyquinoline derivatives are under investigation.

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