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A unique 'ON–OFF–ON' switch with two perturbations at two different concentrations of Ag^+

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Abstract—The dipod 1,2-bis(8-quinolinoxymethyl)benzene **3** and tetrapod 1,2,4,5-tetrakis(8-quinolinoxymethyl)benzene **4** show two perturbations in fluorescence with Ag^+, (i) fluorescence quenching with <1.0 equiv of $AgNO_3$ at λ_{max} 395 nm and (ii) fluorescence enhancement at λ_{max} 500 nm with >3 equiv of $AgNO_3$. This 'ON–OFF–ON' switching of **3** and **4** in comparison with simultaneous fluorescence quenching and enhancement in the case of 8-methoxyquinoline **1** and the tripod 1,3,5-trimethyl-2,4,6-tris(8-quinolinoxymethyl)benzene **2** point to the unique role of molecular architectures arising due to the number and spatial positions of quinoline units in the fluorescence behaviour of an 8-alkoxyquinoline moiety towards Ag^+.

The design and synthesis of target selective receptors with luminescent signalling systems for direct measurement of changes in emission intensities, wavelength or excited life time, 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 the total free energies of the system.[3] So, in addition to the complementarity of binding sites, the spatial placement of subunits[4] constitutes the major criteria for designing new receptors.

8-Hydroxyquinoline and its derivatives are known to be the best chelators after EDTA and its derivatives, due to their guest modulated chromogenic and fluorescent behaviour. Accordingly, they have attained prime significance and have been used in chromatography,[5] detection of metal ions,[6] in organic light emitting diode devices[7] and in electrochemiluminescence,[8] etc. In the case of planar platforms, in all investigations, the contribution of molecular architectures arising due to the 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.[9] However, the supramolecular behaviour of receptors possessing two and four such functional groups placed symmetrically at 1,2-, or 1,2,4,5-positions of a benzene ring has been scarcely studied.[10]

In the present work, we report that the sterically crowded 1,2-dipod **3** and 1,2,4,5-tetrapod **4** (Fig. 1) undergo fluorescence quenching with <1.0 equiv of Ag^+ (λ_{max} 350 nm) and fluorescence enhancement (λ_{max} 500 nm) with >3 equiv of Ag^+. This provides a unique

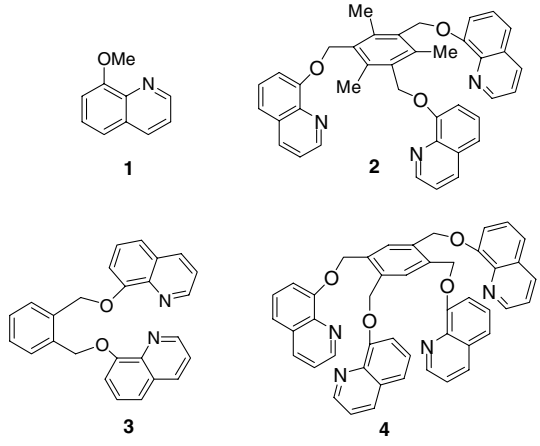

Figure 1. Structures of podands **1**–**4**.

Keywords: Hydroxyquinoline; Tetrapod; Fluorescence; Selective perturbation.
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possibility for the measurement of two different concentrations of Ag^+ with one compound due to two perturbations at different wavelengths. This points to the role of the spatial architectures of 8-hydroxyquinoline moieties, placed at different positions on a benzene platform, on their Ag^+ modulated fluorescence behaviour.

1,2,4,5-Tetrakis(8-quinolinoxymethyl)benzene **4**[11] and 1,2-bis(8-quinolinoxymethyl)benzene **3**[12] were prepared by refluxing 8-hydroxyquinoline with 1,2,4,5-tetrakis(bromomethyl)benzene[13] and 1,2-bis(bromomethyl)-benzene[14] under phase transfer catalyzed conditions. 8-Methoxyquinoline **1** and tripod **2** were prepared by the reported procedures.[15] The assignment of ^1H signals in **3** and **4** were made from decoupling and ^1H–^1H COSY spectral data.

Receptors **1**–**4** (10 μM, CH_3CN) exhibit a broad absorption band at λ_{max} 305 nm and on excitation at λ_{max} 305 nm exhibit fluorescence at λ_{max} 390 ± 5 nm, which is typical of 8-hydroxyquinolines. The fluorescence maxima of **1**–**4** do not undergo any change within λ_{ex} 250–350 nm. Also, at least in the concentration range 1–10 μM, the linear increase of fluorescence with increase in concentration indicates that **1**–**4** are not susceptible to self-quenching or to aggregation processes. In the present work, all studies were performed using λ_{ex} 345 nm.

A solution of 8-methoxyquinoline **1** (10 μM, CH_3CN), on addition of $AgNO_3$, underwent simultaneous quenching at λ_{max} 395 nm and enhancement at λ_{max} 500 nm, up to 100 μM of $AgNO_3$, and then a plateau was achieved at λ_{max} 395 nm. The spectral fitting of the data shows that **1** forms Ag^+·**1** and $2Ag^+$·**1** complexes in acetonitrile with values for $\log \beta_{ML} = 6.5 \pm 0.3$ and $\log \beta_{M_2L} = 11.0 \pm 0.3$. With 1.0 equiv of $AgNO_3$ formation of the Ag^+·**1** complex (81%) is preferred but with 10 equiv of $AgNO_3$, the formation of the $2Ag^+$·**1** complex (72%) is predominant over Ag^+·**1** complex (28%).

Similarly, a solution of tripod **2** (1 μM, CH_3CN) showed simultaneous fluorescence quenching at λ_{max} 395 nm and enhancement at λ_{max} 500 nm on addition of $AgNO_3$. The spectral fitting of the data shows the formation of $2Ag^+$·**2** ($\log \beta_{M_2L} = 10.9 \pm 0.1$) and $3Ag^+$·**2** ($\log \beta_{M_3L} = 15.3 \pm 0.2$) complexes (Table 1). With 10 equiv of $AgNO_3$ mainly (L–M_2L–M_3L = 12:76:12) M_2L exists, which on increasing Ag^+ concentration shifts towards M_3L. With 100 equiv of $AgNO_3$, the solution consists of nearly 60% M_3L and 40% M_2L.

A solution of dipod **3** on excitation at λ_{ex} 345 nm showed a gradual decrease in fluorescence on addition of

Table 1. The $\log \beta_{M_xL}$ values of Ag^+ complexes with podands **1**–**4**

Podand	$\log \beta_{ML}$	$\log \beta_{M_2L}$	$\log \beta_{M_3L}$	$\log \beta_{M_4L}$
1	6.5 ± 0.3	11.0 ± 0.3		
2		10.9 ± 0.1	15.3 ± 0.2	
3	6.3 ± 0.2	9.5 ± 0.2		
4	6.8 ± 0.2	12.2 ± 0.3		17.3 ± 0.6

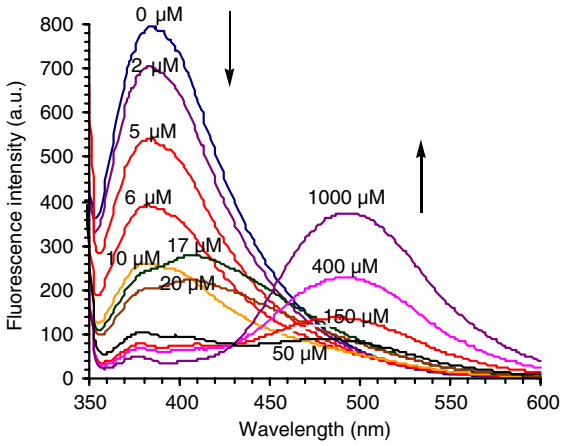

Figure 2. The effect of Ag^+ on the fluorescence behaviour of dipod **3** (10 μM).

$AgNO_3$, which gradually increased on increasing the concentration of $AgNO_3$ (Fig. 2). A plot of concentration of $AgNO_3$ versus fluorescence at 385 nm shows a linear decrease with up to 50 μM $AgNO_3$ (5 equiv) and then a plateau is achieved. During addition of $AgNO_3$, between 10 and 30 μM (1–3 equiv), no significant change in fluorescence at 395 or 500 nm was observed. However, on further addition of $AgNO_3$, a fluorescence band at λ_{max} 500 nm appeared and its intensity gradually increased with an increase in the concentration of $AgNO_3$.

The spectral fitting of the titration data of dipod **3** with $AgNO_3$ shows the formation of ML and M_2L complexes with $\log \beta_{ML} = 6.3 \pm 0.2$ and $\log \beta_{M_2L} = 9.5 \pm 0.2$. Analysis of the distribution of different species showed that their concentration varied significantly with the concentration of Ag^+. In a 1:2 mixture of **3** and $AgNO_3$, an almost maximum concentration of a 1:1 complex (94%) was observed. At this concentration, nearly 1% of a 2:1 $2AgNO_3$·dipod **3** was observed. On further increasing the concentration of Ag^+ to 1000 μM, the formation of M_2L increased to 60% along with 40% of the ML complex.

A solution of tetrapod **4** (10 μM, CH_3CN), on addition of $AgNO_3$ showed fluorescence quenching, which gradually increased with increasing concentration of $AgNO_3$. A plot of concentration of $AgNO_3$ versus fluorescence at 395 nm showed a linear decrease with up to 15 μM $AgNO_3$ (1.5 equiv) and then a plateau was achieved. On addition of further $AgNO_3$, a new fluorescence band emerged at λ_{max} 495 nm. The fluorescence intensity at 495 nm gradually increased with increased concentration of $AgNO_3$. The spectral fitting of the data showed the formation of ML, M_2L and M_4L complexes (Figs. 3 and 4) with $\log \beta_{ML} = 6.8 \pm 0.2$, $\log \beta_{M_2L} = 12.2 \pm 0.3$, and $\log \beta_{M_4L} = 17.3 \pm 0.6$. Analysis of the distribution of the different species showed that their concentration varied significantly with the concentration of Ag^+. In a 1:1 mixture of **4** and $AgNO_3$, an almost maximum concentration of a 1:1 complex (>75%) is observed. At this concentration, nearly 10% of the 2:1 $2AgNO_3$·tetrapod **4** is formed. On further increasing the concentration of

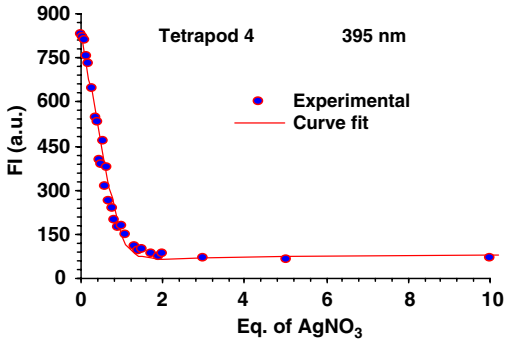

Figure 3. The curve fitting of fluorescence spectral data of **4** at 395 nm on addition of $AgNO_3$: (O) experimental points, (--) fitted line.

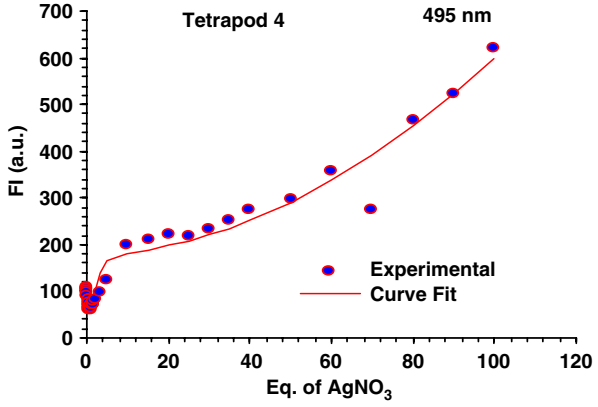

Figure 4. The curve fitting of fluorescence spectral data of **4** (10 μM in CH_3CN) at 495 nm on addition of $AgNO_3$: (O) experimental points, (--) fitted line.

Ag^+ to 200 μM, the formation of M_2L increases to 97% along with <1% of a 4:1 $4AgNO_3$·tetrapod **4** complex. Even at 1000 μM $AgNO_3$, the 4:1 $4AgNO_3$·tetrapod **4** complex is formed to 11% extent only along with 89% of a 2:1 complex. Due to the existence of a number of different stoichiometric complexes of **4** with Ag^+, isosbestic points were not observed.

In summary, 1,2-dipod **3** and 1,2,4,5-tetrapod **4**, on addition of <1 equiv of $AgNO_3$ undergo 'switch off' at λ_{max} 395 nm, then between 10 and 30 μM do not show any significant change in fluorescence intensities, and then at >30 μM $AgNO_3$ concentrations 'switch on' of the fluorescence with a red shift to 495 nm is observed. The lack of such delayed fluorescence enhancement with the addition of $AgNO_3$ to the solutions of monopod **1** and 1,3,5-tripod **2** suggests that in the case of **3** and **4**, the placement of the quinoline units closer to each other leads to more crowded architectures, which inhibit some of the interaction modes of quinoline with Ag^+ but, later, with the availability of higher concentrations of $AgNO_3$, delayed fluorescence reappears. This phenomenon enables estimation of $AgNO_3$ between two different concentration ranges with the same molecule.

A plot of the number of quinoline units/Ag^+ cation versus concentration of Ag^+ shows that both **3** and **4**

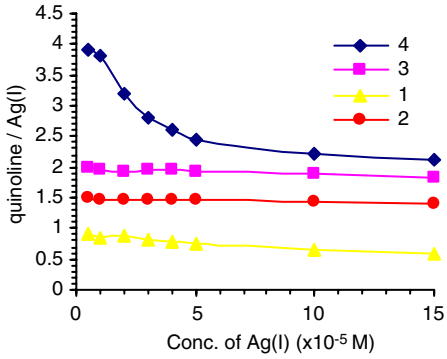

Figure 5. The plot of number of quinoline units per Ag^+ in podands **1**–**4**.

organize higher numbers of quinoline units around Ag^+ than in the case of 8-methoxyquinoline **1** and tripod **2** (Fig. 5). At less than 5 equiv of $AgNO_3$, the tetrapod **4** shows significantly higher numbers of quinoline units around Ag^+ than in the case of **3**, which in turn shows a higher order of quinolines per Ag^+ than in the cases of **1** and **2**. All these results clearly point to the organization of four quinoline units around Ag^+ in the case of **4**, at least at <5 equiv of Ag^+.

Therefore, podands **1**–**4** exhibit different fluorescence perturbations with Ag^+ and point to the role of the spatial placement of quinoline moieties in achieving different modulations.

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11. A solution of 8-hydroxyquinoline (850 mg, 5.5 mmol), NaH (pre-washed with hexane) (275 mg, 11.4 mmol) and tetrabutylammonium hydrogen sulfate (20 mg) (catalyst) in DMF (30 ml) was stirred at 80 °C. After 30 min, 1,2,4,5-tetrakis(bromomethyl)benzene (500 mg, 1.1 mmol) was added and stirring was continued at 80 °C. After completion of the reaction (TLC, 24 h), the solid residue was filtered off and was washed with ethyl acetate. The combined filtrate was evaporated under vacuum and the solid residue was purified by column chromatography over silica-gel (60–120 mesh) using a mixture of CH_2Cl_2–ethyl acetate–MeOH (80:17:3, v/v) to obtain pure **4**, as a white solid (40%). Mp 233–237 °C (CH_3CN–$CHCl_3$), FAB mass *m*/*z* 707 (M^++H); ^{1}H NMR ($CDCl_3$) (300 MHz): δ 5.62 (s, 4×CH_2, 8H), 7.00 (d, $J = 7.2$ Hz, 4H, 4×HQ-H7), 7.19–7.30 (m, 8H, 4×HQ-H6, 5), 7.37 (dd, $J_1 = 8.1$ Hz, $J_2 = 4.2$ Hz, 4H, 4×HQ-H3), 7.80 (s, 2H, ArH), 8.06 (d, $J = 6.9$ Hz, 4H, 4×HQ-H4), 8.86 (d, $J = 2.7$ Hz, 4H, 4×HQ-H2); ^{13}C NMR ($CDCl_3$–DMSO-d_6) (75 MHz) (normal/DEPT-135): δ 67.36 (−ve, CH_2), 112.5 (+ve, ArCH), 119.0 (+ve, ArCH), 119.1 (ab, ArC), 121.1 (+ve, ArCH), 128.2 (ab, ArC), 128.3 (+ve, ArCH), 128.5 (+ve, ArCH), 133.4 (ab, ArC), 143.2 (+ve, ArCH), 144.5 (+ve, ArCH), 147.2 (ab, ArC). Found: C, 77.93; H, 4.70; N, 7.90%. $C_{46}H_{34}N_4O_4$ requires C, 78.17; H, 4.85; N, 7.93%.
12. The reaction of 8-hydroxyquinoline with 1,2-bis(bromomethyl)benzene using the above procedure provided **3** (48%); as a white solid, mp 112–115 °C (CH_3CN), FAB mass *m*/*z* 392 (M^++H): ^{1}H NMR ($CDCl_3$) (300 MHz): δ 5.62 (s, 2×OCH_2, 4H), 7.12 (dd, $J_1 = 5.8$ Hz, $J_2 = 3.0$ Hz, 2H, ArH), 7.27–7.34 (m, 6H, 2×HQ-H6, 5, 7), 7.39 (dd, $J_1 = 8.4$ Hz, $J_2 = 3.9$ Hz, 2H, 2×HQ-H3), 7.59 (dd, $J_1 = 5.7$ Hz, $J_2 = 3.3$ Hz, 2H, ArH), 8.08 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 2H, 2×HQ-H4), 8.92 (dd, $J_1 = 4.2$ Hz, $J_2 = 1.8$ Hz, 2H, 2×HQ-H2); ^{13}C NMR ($CDCl_3$) (75 MHz) (normal/DEPT-135): δ 69.1 (−ve, CH_2), 110.0 (+ve, ArCH), 119.8 (+ve, ArCH), 121.5 (+ve, ArCH), 126.5 (+ve, ArCH), 128.2 (+ve, ArCH), 128.7 (+ve, ArCH), 129.4 (ab, ArC), 134.9 (ab, ArC), 135.7 (+ve, ArCH), 140.5 (ab, ArC), 149.2 (+ve, ArCH), 154.2 (ab, ArC). Found: C, 79.30; H, 5.40; N, 6.90%. $C_{26}H_{20}N_2O_2$ requires C, 79.57; H, 5.14; N, 7.14%.
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