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A novel dansyl-appended glycoluril-based fluorescence sensor for silver ions

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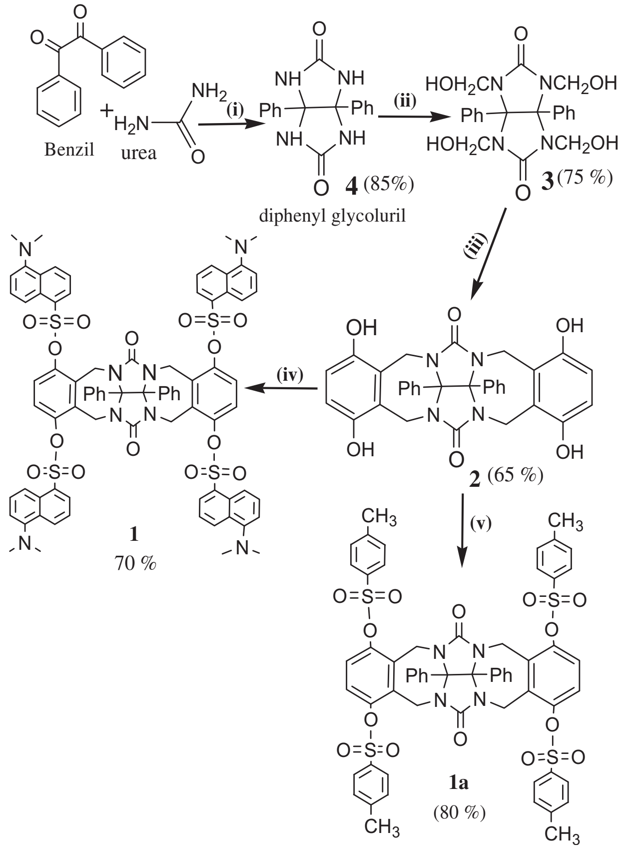
ABSTRACT

Tetra-dansylated diphenyl glycoluril has been synthesized and evaluated for ionic recognition. The synthesized molecular receptor shows selective response to silver ions as determined through the enhancement of fluorescence intensity.

Recently, among numerous macrocycles, glycoluril-based molecular receptors have garnered immense attention.[1–3] This is mainly due to their rigid skeleton, high melting point, and potentially significant multiple hydrogen bond donative (NH) and acceptive (C=O) molecular characteristics.[4–8] Since fluorescence spectroscopy offers a sensitive detection technique for ionic and molecular species,[9,10] we decided to introduce a fluorophore in a glycoluril backbone (**1**) to achieve an on/off type chemosensor for ionic recognition. Though most reported chemosensors for heavy/transition metal ions are based upon quenching of fluorescence intensity ('turn off')[11] only a few are based upon enhancement of fluorescence intensity ('turn on').[12] The latter type of chemosensors are both desired and preferred due to their better overall signal processing in biosystems[12] and specificity of mode of action. We report herein a novel glycoluril-based 'turn-on' type fluorescence chemosensor **1** which can recognize silver ions from amongst lithium, sodium, nickel, zinc, copper, mercury, lead, cobalt, cadmium, iron, and chromium.

Compound **1** was obtained in 70% yield from benzil and urea[4a,6] through a series of reactions presented in Scheme 1. It was characterized by ^{1}H and ^{13}C NMR and ESI-TOF MS analysis.[13] When a dilute solution of **1** (20 μM) in acetonitrile (ACN) was excited at 350 nm,[14,15] it exhibited a fluorescence emission band with a maximum at 550 nm.

Compound **1** showed good solvatochromism as its emission maxima were red shifted with increasing solvent polarity (except chloroform) (Supplementary data, Fig. S1). Addition of varying concentrations of metal ions (Ag^+, Li^+, Na^+, Ni^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Fe^{3+}, and Cr^{3+}) revealed an increase of 71% in the presence of 67 μM Ag^+ (Fig. 1). In the presence of most other metal ions the percent enhancement in the fluorescence intensity of **1** was insignificant in comparison to Ag^+ ions. The addition of the same



Scheme 1. Synthesis of tetra-dansylated glycoluril **1** and reference compound **1a**. Reagents and conditions: (i) EtOH, concd HCl, refluxing; (ii) paraformaldehyde, room temperature stirring, N_2 atm; (iii) *p*-toluene sulfonic acid, excess hydroquinone, reflux; (iv) dansyl chloride, Et_3N, stirring; (v) *p*-toluene sulphonyl chloride, Et_3N, stirring.

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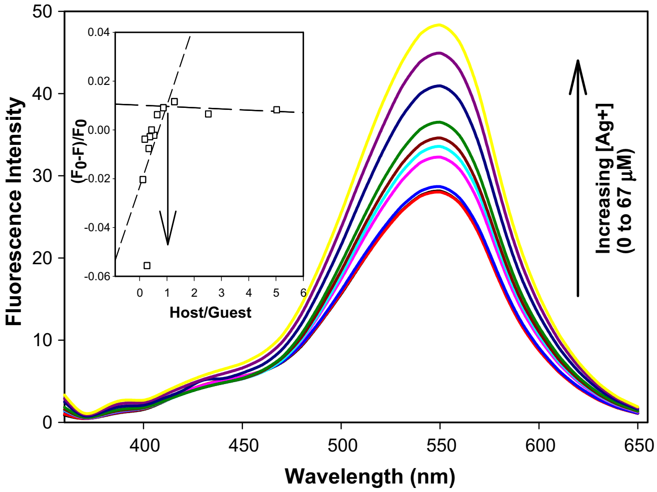

Figure 1. Fluorescence enhancement of **1** in the presence of increasing [Ag$^+$] in acetonitrile at ambient conditions ([**1**] = 20 µM, $\lambda_{\text{excitation}}$ = 350 nm). Inset of the figure represents $\frac{F_0-F}{F}$ versus the mole ratio of the host-to-guest clearly showing the stoichiometry of the complexation to be 1:1. ([**1**] = 20 µM, $\lambda_{\text{excitation}}$ = 350 nm).

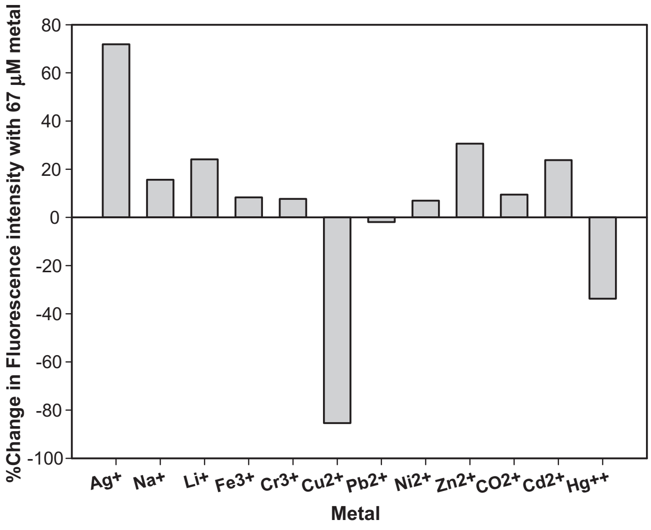

Figure 2. Percent change in fluorescence intensities of **1** (20 µM) in the presence of 67 µM of various metal ions in acetonitrile (perchlorate salts are used).

concentration of Cu^{2+}, Hg^{2+}, and Pb^{2+} led to the quenching of fluorescence intensity of **1** (Fig. 2). Control experiments with dansyl chloride revealed that severe quenching of **1** in the presence of Cu^{2+} was due to the heavy metal effect through collisional quenching.[14]

A plot of $\frac{F_0-F}{F}$ versus the mole ratio of [**1**]-to-[Ag$^+$] revealed that they interact in a 1:1 stoichiometric manner (where F_0 and F are the fluorescence intensities in the absence and the presence of [Ag$^+$], respectively (inset of Fig. 1)) with an equilibrium constant of 224(±15) M^{-1} (for $\mathbf{1} + \text{Ag}^+ \rightleftharpoons \mathbf{1}\cdot\text{Ag}^+$) (calculations are provided in Supplementary data). Reference compound **1a** was also synthesized. It was observed that there was an insignificant enhancement in the fluorescence intensity of **1a** in the presence of varying concentrations of Ag$^+$ (Supplementary data, Fig. S2). Again when the same experiments were repeated with dansyl chloride alone, a small decrease in the fluorescence intensity was observed (data not shown). NMR titration experiments (Supplementary data, Fig. S3) revealed that the dan-H signal shifts upfield while those of N–CH$_2$ protons shift downfield on the addition of Ag$^+$ to the host **1** in CDCl$_3$ indicating the close proximity of Ag$^+$ to the dansyl aromatic framework through a plausible cation π-type interaction. It appears that the Ag$^+$ imparts certain rigidity to the dansyl moieties on the glycoluril framework. Apparently, the interaction of Ag$^+$ with the dansyl moiety decreases the rate of non-radiative deactivation pathways by facilitating the twisted intra-molecular charge transfer (TICT) process to result in the fluorescence intensity enhancement.

In conclusion, we have achieved a novel 'turn on' type glycoluril-based fluorescence sensor for silver ions. Further work to understand the exact sensing mechanism is in progress.

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Supplementary data

Supplementary data (Figs. S1–S3 and calculation for equilibrium constant) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.07.005.

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13. Compound **1**: Pale yellow solid, yield: 70%, mp 260–262 °C; UV (λ_{max}, CH$_3$CN): 256, 350 nm. IR (KBr pellet, cm^{-1}): 1575, 1366, 1310, 1184, 1133, 1061. ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 8.56 (4H, d, dan-*H*), 8.55 (4H, d, dan-*H*), 7.97 (4H, d, dan-*H*), 7.60 and 7.45 (8H, t, dan-*H*), 7.18 (4H, d, dan-*H*), 7.16-6.94 (m, 10H, Ph-*H*), 6.09 (s, 4H, Ar-H), 5.39 (d, 4H, ArCH_2Ar), 3.72 (d, 4H, ArCH_2Ar), 2.85 (s, 24H, N(CH_3)$_2$). ^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 156.7, 151.7, 145.3, 133.9, 132.6, 131.0, 129.8, 129.6, 129.3, 122.8, 119.6, 115.8, 99.9, 84.7, 45.4, 38.2, 29.7; HRMS (ESI-TOF) *m*/*z*: calcd 1495.3900, found 1495.3552 [M$^+$+1]; **1a**: light brown solid, yield: 80%, mp 222–225 °C; UV (λ_{max}, CH$_3$CN): 274 nm. IR (KBr pellet, cm^{-1}): 1596, 1461.6, 1377.9, 1261.8, 1192.9, 1091.1; ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 7.68 (8H, d, tosyl-*H*), 7.25 (8H, d, tosyl-*H*), 7.06–6.89 (m, 10H, Ph-*H*), 6.62 (s, 4H, Ar-H), 5.19 (d, 4H, ArCH_2Ar), 3.59 (d, 4H, ArCH_2Ar), 2.34 (s, 12H, CH_3); HRMS (ESI-TOF) *m*/*z*: calcd 1179.3212, found 1179.3646 [M$^+$].
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