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A Versatile and Conformationally Adaptable Fluorene-Based Receptor for Efficient Binding of Silver Cation

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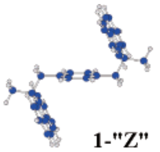
Intermolecular noncovalent binding of silver cation by synthetic macromolecular receptors continues to attract considerable attention.[1] Importantly, the focus has been to design molecular systems that bear two or more aromatic groups in cofacially oriented arrays (such as *cis*-diarylalkenes, cyclophanes, triptycenes, deltaphanes, cylinderophanes, etc.)[2] as electron donors for the preparation of metal ion aromatic donor−acceptor complexes for the potential applications in the areas of electrical conductors and photoresponsive devices.[3] Despite numerous ingenious designs of novel receptors, including the ones containing fluorescent sensing units,[4] need remains for a readily available and versatile receptor that can bind silver cation effectively and should allow its eventual incorporation into a polymeric backbone for practical applications in the emerging area of molecular electronic and nanotechnology.[5]

Density functional theory (DFT) calculations[6] at the B3LYP/6-31G* level led us to the hitherto unknown hydrocarbon ligand 1,4-bis(9-methyl-9*H*-fluoren-9-yl)methyl]benzene (**1**) that potentially meets the criteria of ready availability and possible incorporation into a polymeric structure. Our interest in this receptor stems from the fact that it possesses the unique molecular structure where a simple C−C single bond rotation converts it from an extended ("**Z**") conformer to an isoenergetic[6] (folded) delta ("**Δ**") conformer. The cavity formed by three aromatic walls (i.e., two fluoranyl rings and one *p*-xylyl ring) in the **Δ** conformer of **1** is remarkably similar to that found in π-prismand (**2**)[7a] (or a structurally analogous deltaphane[7b]) — a well-known and efficient receptor for the silver cation, as shown below:



1-"Z"

1-"Δ"

2

Accordingly, in this report, we will describe a simple (one-pot) preparation of (thus far unknown) conformationally adaptable receptor **1** from *readily available* and cheap precursors and delineate that it binds a single silver cation (Ag^+) with remarkable efficiency that exceeds the binding abilities of well-known π-prismand **2** by at least 2 orders of magnitude. The binding of a single silver cation with this versatile fluoranyl-based receptor was monitored by ^1H NMR and UV−vis spectroscopy, and the results are compared with a model compound (**3**) containing only one fluoranyl moiety as follows.

The receptor **1** and its model compound **3** were easily prepared in multigram quantities, in a one-pot procedure, in a matter of hours according to the Scheme 1. Thus, a reaction of fluoranyl anion, generated using *n*-BuLi at −78 °C, with iodomethane followed by further lithiation and a reaction with α,α-dichloro-*p*-xylene and α-chloro-*p*-xylene afforded **1** and **3**, respectively, in excellent yields. (See Supporting Information for the experimental details and spectral data.)

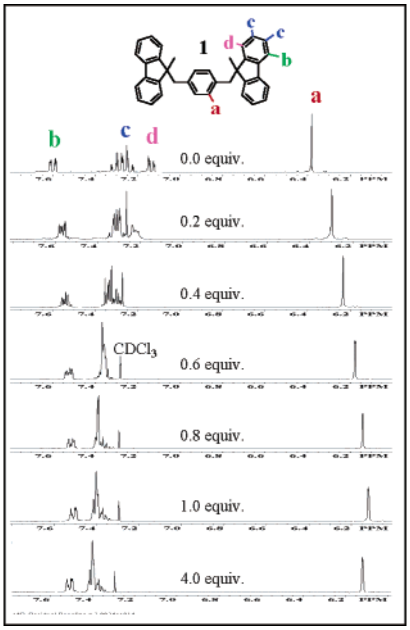
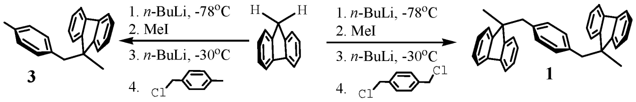


Figure 1. Partial ^1H NMR spectra of **1** obtained upon an incremental addition of CF_3SO_3Ag in $CDCl_3-CD_3OD$ at 22 °C.

Scheme 1. Synthesis of Receptor **1** and Its Model Compound **3**



The binding of silver cation to **1** was initially monitored by the changes in the ^1H NMR spectrum of **1** in chloroform-*d* (0.05 mM) by an incremental addition of a solution of silver trifluoromethanesulfonate (0.5 mM) in methanol-d_4. The addition of the increments of Ag^+ solution showed considerable shifts of the aromatic signals up to the addition of 1 equiv of Ag^+, as shown in Figure 1. It is noteworthy that the ^1H NMR spectrum remained unchanged upon further addition of Ag^+ solution (i.e., beyond 1 equiv). Unfortunately, an accurate binding constant for the formation of [**1**, Ag^+] could not be determined by NMR method as it simply showed complete capture of the Ag^+ and suggested that the binding constant is too large to be measured by NMR spectroscopy. It is, however, noteworthy that a similar ^1H NMR spectral titration of a solution of model donor **3**, containing only one fluoranyl unit, with Ag^+ (under identical conditions) showed that it binds Ag^+ with much less efficiency and required a large excess of Ag^+ (>50 equiv) for complete utilization of the ligand and gave a binding constant[2b] $K = 10 \pm 5$ M^{-1} for the formation of [**3**, Ag^+].

The binding of silver cation to **1** can also be easily monitored by UV−vis spectroscopy, as shown in Figure 2. Thus, an incremental addition of a solution of silver trifluoromethanesulfonate in methanol (15 mM) to a solution of **1** in dichloromethane (0.8

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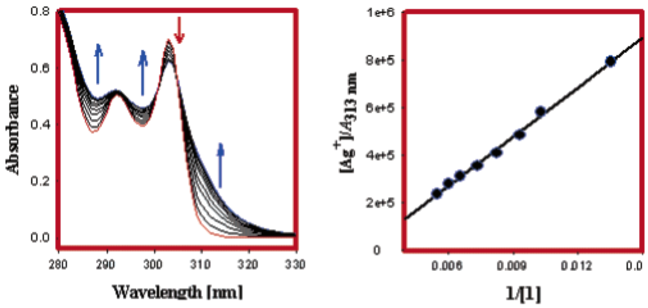


Figure 2. (Left) Spectra obtained upon the incremental addition of a solution of $Ag^+CF_3SO_3^-$ in methanol (black) to a solution of **1** (red) in $CHCl_3$ at 22 °C. (Right) Benesi−Hildebrand plot of **1** and $Ag^+CF_3SO_3^-$.

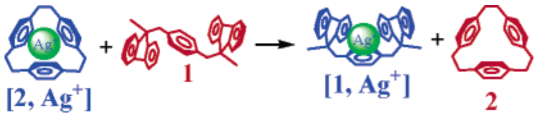
mM) showed the growth of a new absorption band in the UV−vis absorption spectra up to the addition of 1 equiv of a solution of Ag^+. [Note that the UV−vis spectrum remained unchanged upon further addition of Ag^+ solution (i.e., beyond 1 equiv).] To determine the binding constant for the formation of the [**1**, Ag^+] complex, in a separate experiment, the absorbance changes were measured at 313 nm (A_{313}) as a function of the increments of added receptor [**1**] to a solution of 0.6 mM Ag^+ in a $CHCl_3-CH_3OH$ (9:1) mixture and were treated by the Benesi−Hildebrand procedure[8] (i.e., eq 1).

$$\frac{[Ag^+]}{A_{313}} = \frac{1}{\epsilon_{313}} + \frac{1}{K\epsilon_{313}}\frac{1}{[\mathbf{1}]} \qquad (1)$$

where A_{313} is the molar absorbance and ϵ_{313} is the extinction coefficient of the new absorption band (tentatively assigned as charge-transfer absorption band). For Ag^+ concentrations much greater than that of receptor (**1**), a plot of $[Ag^+]/A_{313}$ versus the reciprocal receptor concentration was linear, and the least-squares fit produced a correlation coefficient of greater than 0.99 as shown in Figure 2 (right). From the slope and the intercept, the values of the association constant (K) and the extinction coefficient (ϵ_{313}) were readily extracted as 15 000 ± 800 M^{-1} and 2100 ± 100 M^{-1} cm^{-1}, respectively.

It is important to note that a 1:1 complexation stoichiometry for the [**1**, Ag^+] complex was established by Job's plot analysis,[9] where the growth of the absorption band at 313 nm was plotted against mole fractions of **1** under the conditions of a constant total concentration. As such, the concentration of the **1**−Ag^+ complex approached a maximum when the molar fraction of [**1**]/[Ag^+] was about 0.5 (see Figure 3).

The remarkably efficient binding of a single silver cation by the conformationally adaptable receptor **1** was further confirmed by a competition experiment with π-prismand **2**, a well-known receptor for Ag^+ cation.[7] Thus, a chloroform-*d* solution of the [**2**, Ag^+] complex quantitatively transferred its bound silver cation to an equimolar amount of added receptor **1** as established by NMR spectroscopy (see Figure S1 and S2 in the Supporting Information) (i.e., eq 2).



(2)

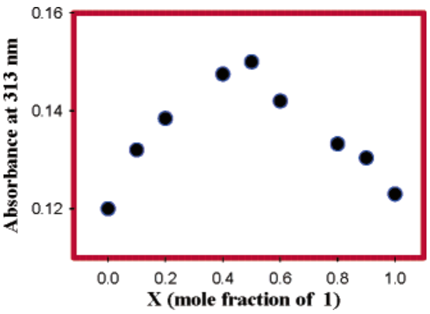


Figure 3. Job's plot of a 1:1 complex of **1** and Ag^+ cation, where the absorption at 313 nm was plotted against the mole fraction of **1** at an invariant total concentration of 1.4×10^{-4} M in a 1:19 mixture of MeOH/$CHCl_3$ (v/v).

As such, this competition experiment allowed us to establish that the receptor **1**, due to its adaptability and conformational flexibility, wraps around a single Ag^+ cation with efficiency that is at least 100 times greater than the that of the π-prismand **2**.[7]

In summary, we have designed and synthesized a simple and conformationally adaptable receptor that binds a single silver cation with remarkable efficiency because of the fact that it readily adapts a deltaphane- or π-prismand-like conformation by a simple C−C bond rotation. The binding event can be easily monitored by ^{1}H NMR and UV−vis spectroscopy. Moreover, it can be easily envisioned that this versatile receptor holds potential to be incorporated into a variety of polymeric backbones by attachments at the carbon 9 of the fluoranyl moieties. We are actively exploring the preparation of such polymeric materials containing multiple receptor sites as well as the selectivity of binding among various metal cations.

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Supporting Information Available: Preparation and spectral data for **1**−**3** and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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