

Charge Transfer Based Colorimetric Detection of Silver Ion

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Donor–acceptor interactions or charge transfer (CT) interactions¹ are an important class of non-covalent interactions and have been widely exploited in self-assembling systems. Beyond molecular chemistry, supramolecular chemistry aims at constituting highly complex, functional chemical systems from components held together by intermolecular forces. Chemosensors are the molecules of abiotic origin that bind selectively and reversibly with the analyte with concomitant change in one or more properties of the system. The recognition and signaling of ionic and neutral species of varying complexity is one of the most intensively studied areas of contemporary supramolecular chemistry.² Among different types of chemosensors, colorimetric/chromogenic chemosensors are especially attractive because the guest determination can be carried out by the naked eye, without the use of expensive equipment and they also find direct applications in the development of optodes and disposable dip-stick arrays based on absorption changes.³ Although molecules containing an electron donor and an electron acceptor linked by a spacer have also been studied extensively in conjunction with the development of stable intramolecular CT complex,^{4,5} to the best of our knowledge, there is no report to sense the analyte using molecules containing an electron donor and an electron acceptor linked by a spacer. In continuation with our research on the self-assembling supramolecular systems *via* donor–acceptor interactions,⁶ we were intrigued to apply this interaction for signaling of ionic species. Herein we report on the design

and synthesis of **U-shape** molecule which is linked by oligoethylene glycols (OEGs) between an electron-deficient (methyl viologen; MV²⁺) and an electron-rich (2,6-dialkoxy-naphthalene; Np) units and their application on sensing metal ion (Figure 1).

Experimental Section

Compound 4. A mixture of 6-methoxy-2-naphthol (128 mg, 0.73 mmol) and compound **3** (500 mg, 0.73 mmol) in acetone (30 mL) in the presence of potassium carbonate (203 mg, 1.46 mmol) was refluxed for 14 h. The resulting mixture was diluted with EtOAc and filtered and the filtrate was concentrated and purified by column chromatography (EtOAc/hexane system) to afford the pure product **4** (215 mg, 40%). This reaction also afforded byproduct which is compound **5**. ¹H-NMR (300 MHz, CDCl₃) δ 3.21 (t, *J* = 6.9 Hz, 2H), 3.62–3.72 (m, 18H), 3.81–3.90 (m, 9H), 4.13–4.14 (m, 4H), 4.18 (t, *J* = 7.8 Hz, 2H), 6.88 (m, 4H), 7.07–7.16 (m, 4H), 7.59 (d, *J* = 3.9 Hz, 1H), 7.62 (d, *J* = 4.0 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃) δ 2.9, 55.1, 67.3, 68.6, 69.5, 70.0, 70.36, 70.45, 70.49, 70.6, 71.7, 105.8, 106.9, 114.7, 118.7, 119.0, 121.4, 127.9, 128.0, 129.4, 129.6, 148.7, 155.0, 155.9; MS (FAB): *m/z* 728.46 [M⁺]; HRMS (FAB): Calcd for C₃₃H₄₅O₁₀: 728.2057. Found: 728.2072 [M⁺], 729.2130 [M⁺+H].

Compound 1. A solution of *N*-methyl-4,4'-bipyridinium iodide (18.3 mg, 0.06 mmol) and compound **4** (53.7 mg,

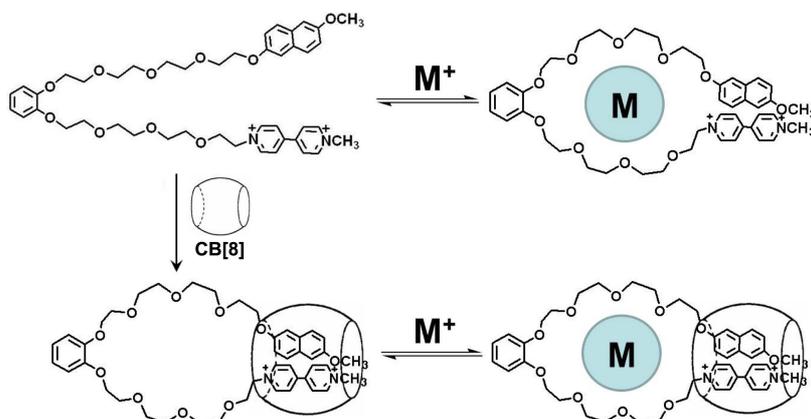


Figure 1. A representative picture showing the possible interaction of sensor with metal ion.

0.07 mmol) in DMF (0.12 mL) was stirred for 2 days at 80 °C and then cooled to room temperature. Then THF was added to precipitate the product. The precipitates were collected by the filter or centrifugation and washed with THF. The solids were dried in vacuum to afford the desired product **1** (61 mg, 95%). ¹H-NMR (500 MHz, D₂O) δ 3.70-3.74 (m, 8H), 3.76-3.82 (m, 12H), 3.88 (s, 3H), 3.90-3.92 (m, 4H), 3.95 (t, *J* = 4.0 Hz, 2H), 4.09 (t, *J* = 4.5 Hz, 2H), 4.13 (br, 2H), 4.37 (s, 3H), 4.84 (t, *J* = 4.5 Hz, 2H), 6.68-6.79 (m, 4H), 6.93 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.5 Hz, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 7.04 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.5 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 2.5 Hz, 1H), 8.03 (d, *J* = 7.0 Hz, 2H), 8.13 (d, *J* = 7.0 Hz, 2H), 8.73 (d, *J* = 6.5 Hz, 2H), 8.96 (d, *J* = 6.5 Hz, 2H); ¹³C-NMR (75 MHz, D₂O) δ 49.2, 55.1, 61.9, 67.2, 68.7, 69.1, 69.5, 70.1, 70.2, 70.4, 70.5, 70.6, 105.4, 106.6, 114.3, 118.3, 118.7, 122.5, 127.1, 127.2, 127.5, 127.6, 129.1, 129.3, 146.4, 146.7, 147.6, 149.6, 150.3, 154.7, 155.6; MS (FAB): *m/z* 899.03 [M⁺-I], 772.21 [M⁺-2I]; HRMS (FAB): Calcd for C₄₄H₅₆I₂N₂O₁₀: 1026.2024. Found: 899.2977 [M⁺-I].

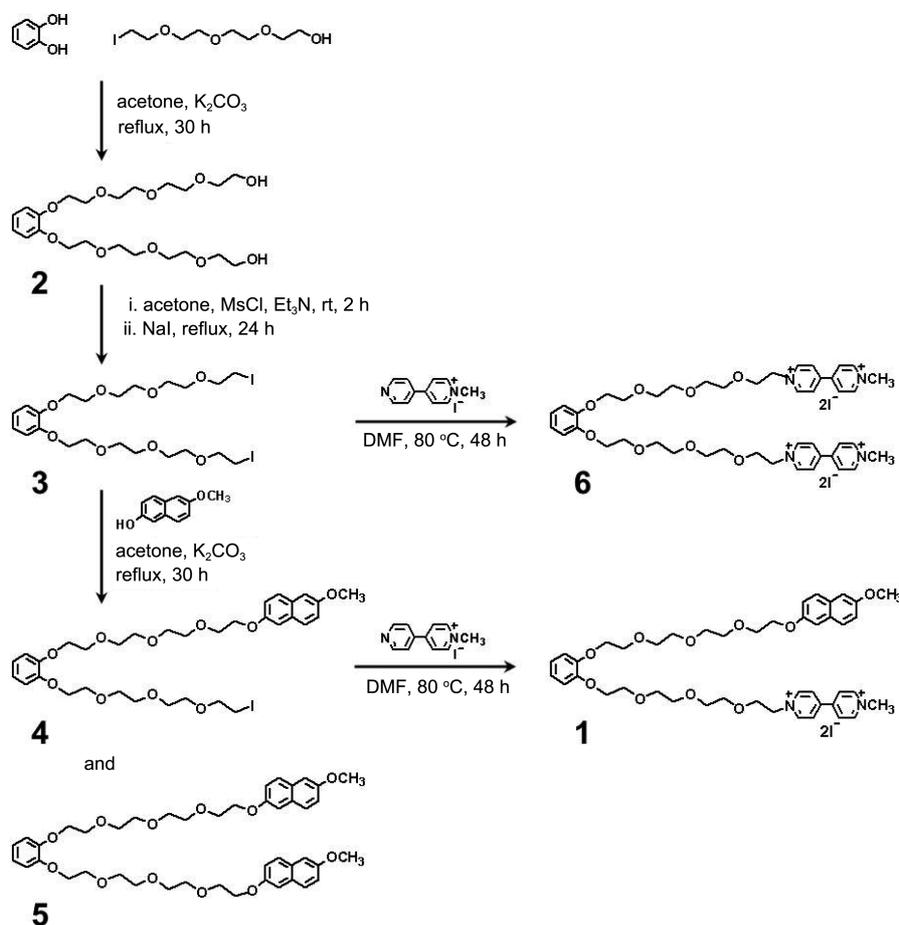
Results and Discussion

An early landmark in the development of receptors for group I metal cations was Pedersen's observations of the formation of side products during the synthesis of 'metal

deactivators' for use in the stabilization of rubber.⁷ The ensuing decade brought further notable advances through the use of the principles of shape and size complementarity which is important key in the design and construction of chemosensors for cations.⁸ In this sensing process, information at the molecular level, such as the presence or not of a certain guest in solution, is amplified to a macroscopic level so that sensing might open the door to qualitative or quantitative determination of certain guests.

The synthesis of U-shape molecule, linked by oligoethylenglycols between an electron-deficient (methyl viologen; MV²⁺) and an electron-rich (2,6-dialkoxy-naphthalene; Np) units, is shown in Scheme 1. Bis-*O*-alkylation of catechol with iodo-tetraethylene glycol afforded compound **2** in 64% yield. Diiodide compound **3** was obtained in yield of 94% by mesylations of diols **2** with MsCl and followed by iodinations with sodium iodide. Nucleophilic displacement of one iodo group in **3** with 6-methoxy-2-naphthol gave compound **4** in 40% yield. Finally, reaction of **4** with 1-methyl-4-(4-pyridyl)-pyridinium iodide provided the desired compound **1** in yield of 95%. The chemical structures of these compounds were confirmed by ¹H- and ¹³C-NMR spectroscopy, IR spectroscopy, and mass spectrometry.

First of all, we examined the host induced intramolecular CT complex. Treatment of 1 equiv of CB[8] into a solution of compound **1** results in a drastic change in the UV/Vis



Scheme 1. Synthesis of compound **1**.

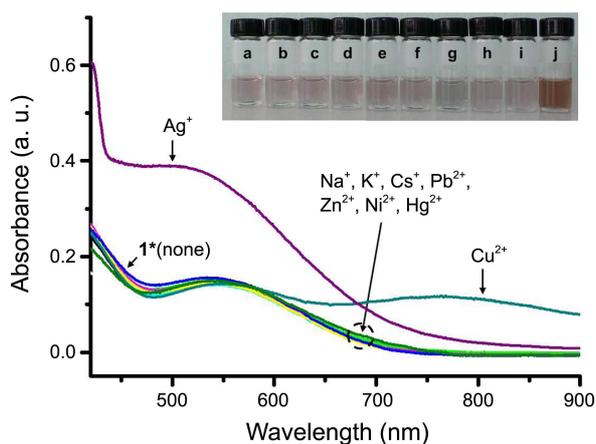


Figure 2. UV-vis spectra of CT complex **1*** upon the addition of various metal ions (5.0×10^{-4} M in H_2O). (a) none, (b) Na^+ , (c) K^+ , (d) Cs^+ , (e) Pb^{2+} , (f) Zn^{2+} , (g) Cu^{2+} , (h) Ni^{2+} , (i) Hg^{2+} , and (j) Ag^+ (10 equiv) were added to each sensor solution. Photograph shows the appearance of the solutions which were allowed to stand for 6 h.

spectrum. The appearance of new absorption bands at $\lambda = 544$ nm supports the formation of the charge transfer complex **1*** between an electron-deficient (methyl viologen; MV^{2+}) and an electron-rich (2,6-dialkoxynaphthalene; Np) units inside the hydrophobic cavity of CB[8].⁹ And then we tried to sense metal ions using CT complex **1***. Figure 2 shows the absorption spectra of **1*** (5.0×10^{-4} M in H_2O) and those in the presence of various metal ions. No significant change in the absorption of CT complex **1*** was observed upon the addition of various metal ions including Na^+ , K^+ , Cs^+ , Pb^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , and Hg^{2+} (10 equiv). However, the charge-transfer complex **1*** shows drastic increase of absorption intensity around 540 nm in the presence of Ag^+ (10 equiv). In addition, the violet of CT complex **1*** in water changed to a reddish brown color upon the addition of Ag^+ . The high selectivity obtained in sensing metal ions by **1*** may be explained by the coordination of Ag^+ with ether oxygen atoms in the OEGs.¹⁰ The selectivity of **1*** for various metal ions evaluated by the color change is photographically presented in Figure 2.

Second, we investigated the possible colorimetric mechanism using compound **1**. The sensing of metal ions using compound **1** was determined by using the UV-visible spectroscopy. Figure 3 shows the absorption spectra of **1** (5.0×10^{-4} M in H_2O) and those in the presence of various metal ions. Before the addition of metal ions, compound **1** shows no absorption band above 500 nm. No significant change in the absorption of compound **1** was observed upon the addition of various metal ions including Na^+ , K^+ , Cs^+ , Pb^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , and Hg^{2+} (10 equiv). However, compound **1** shows an intense absorption around 540 nm in the presence of Ag^+ (10 equiv). Consequently, the yellowish color of compound **1** in water changed to a reddish brown color upon the addition of Ag^+ . The selectivity of compound **1** for various metal ions evaluated by the color change is photographically presented in Figure 3. Furthermore, $^1\text{H-NMR}$

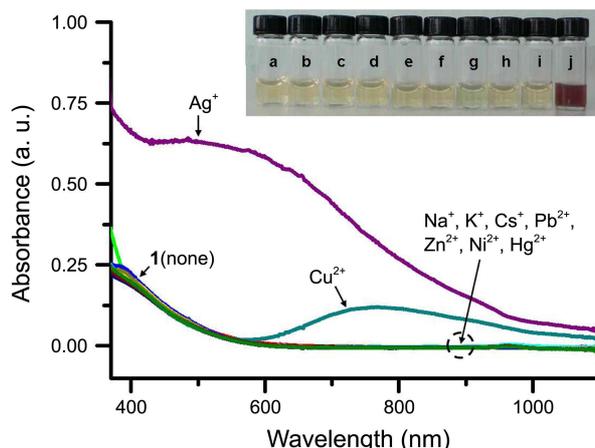


Figure 3. UV-vis spectra of compound **1** upon the addition of various metal ions (5.0×10^{-4} M in H_2O). (a) none, (b) Na^+ , (c) K^+ , (d) Cs^+ , (e) Pb^{2+} , (f) Zn^{2+} , (g) Cu^{2+} , (h) Ni^{2+} , (i) Hg^{2+} , and (j) Ag^+ (10 equiv) were added to each sensor solution. Photograph shows the appearance of the solutions which were allowed to stand for 6 h.

titrations were carried out in CD_3CN to understand further structural characteristics of **1-Ag**⁺ complexes in solution. Upon stepwise addition of Ag^+ , the ^1H signals for OEGs protons present at 3.6–4.0 ppm in the compound **1** were observed further broad result by the coordination of Ag^+ with ether oxygen atoms in the OEGs. And also, the ^1H signals for the Np protons and the viologen protons of compound **1** shift downfield relative to those in the free compound **1** (Figure S1: see supporting information). For the viologen protons, the order of magnitude of the chemical shift variation is Hb ($\Delta\delta$: 0.16 ppm) > Hd (0.15 ppm) > Hc (0.12 ppm) > Ha (0.06 ppm). The chemical shift variation seems to be caused by magnetic anisotropy effect of the Np and viologen units interaction.

The absorption titration spectra of **1** (5.0×10^{-4} M) upon the addition of Ag^+ in H_2O are shown in Figure 4. As shown

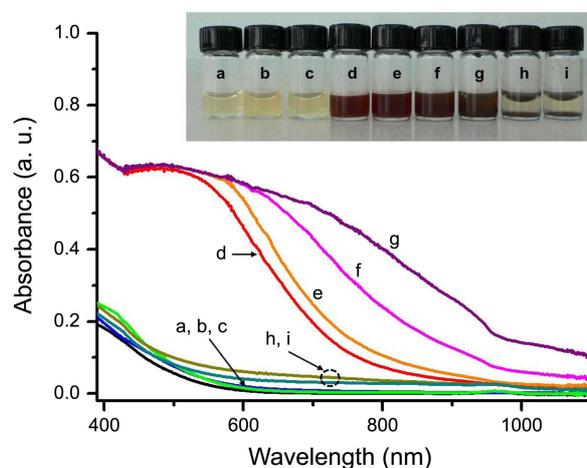


Figure 4. UV-vis spectra of compound **1** upon the addition of Ag^+ (5.0×10^{-4} M in H_2O). (a) none, (b) 1eq, (c) 2eq, (d) 5eq, (e) 10eq, (f) 20eq, (g) 50eq, (h) 100eq, and (i) 150eq were added to each sensor solution. Photograph shows the appearance of the solutions which were allowed to stand for 6 h.

in Figure 4, the addition of Ag^+ (1-2 equiv) had no obvious effect on the absorption band. In the case of 1-2 equiv of Ag^+ , iodide anions (2 equiv) of the viologen unit in a solution of compound **1** lead to the formation of AgI . Thus, the addition of Ag^+ (1-2 equiv) had no dramatic color change to a reddish brown color. However, when 5-50 equiv of Ag^+ were added to the solution of **1**, dramatic color change was observed, suggesting that compound **1** might show specific response with Ag^+ due to the chelation enhanced intramolecular CT interaction from Np to viologen moiety of compound **1**. And another important reason for the color change to a reddish brown color, because it predicts that Ag nanoparticles are formed. Previous study (Li *et al.*) have shown that the Ag nanoparticles contribute to the absorption bands at 450-550 nm in the UV-Vis spectra.¹¹ The absorption titration study shows that the absorption intensity increases as the concentration of AgNO_3 increases, which reflects in the formation of more **1**- Ag^+ complexes and Ag nanoparticles. While in the case of Ag^+ with 100-150 equiv, color change for sensing of Ag^+ was observed and the appearance of new absorption bands around 540 nm supports formations of **1**- Ag^+ and Ag nanoparticles. However, at a high concentration of AgNO_3 (100-150 equiv), the solutions which were allowed to stand for 6 h returned to yellowish color and had no absorption band above 500 nm. It is further noted that increasing the concentration of AgNO_3 gradually during the preparation of charge-transfer complexes led to the formation of nanoparticles and then the particles' size was increased and precipitated over time. Oligoethylene glycols (OEGs) was chosen to present ether oxygen atoms available for sensing of metal ions by the coordination as flexible recognition moiety. OEGs is also a good stabilizer for Ag nanoparticles based on the conclusions made by several research studies.¹² In one of these research works, Luo *et al.* reduced AgNO_3 in the presence of OEGs. In this process, Ag^+ was successfully reduced to Ag^0 to form Ag nanoparticles. This shows that the reduction of the silver ions to silver atoms was continued and resulted in an increase in the concentration of Ag nanoparticles.¹³ In order to study possible mechanism of the formation of Ag nanoparticles, the compound **2**, **5**, and **6** in water with Ag^+ (1-150 equiv) were conducted to examine the color change. When 1-150 equiv of Ag^+ were added to the solutions of compound **2**, **5**, and **6**, dramatic color change and formation of nanoparticles weren't observed. Therefore, in order to the formation of Ag nanoparticles are required to CT interaction between an electron-deficient and an electron-rich units in the presence of OEGs.

In summary, we have demonstrated the colorimetric chemosensor for detection of Ag^+ via formation of nanoparticles which is based on the intramolecular CT interaction between the electron-rich (2,6-dialkoxynaphthalene; Np) moiety and the electron-deficient (methyl viologen; MV^{2+}) moiety of a single sensor molecule. Under irradiation of light, Ag^+ was reduced to very small silver nanoparticle by CT interaction in the presence of OEGs as flexible recognition moiety of

Ag^+ and stabilizer for Ag nanoparticles, thus Ag nanoparticles resulted to reddish brown in the color change of sensor solution, gradually. Therefore, the charge-transfer interaction between an electron-deficient and an electron-rich units existing at a sensor molecule can be regarded as a new and efficient method to construct various colorimetric chemosensors.

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Supporting Information. General methods, characterization data of compounds **2**, **3**, **5**, and **6**, CT complex **1***, and Figure S1.

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