

Fullerene (C₆₀)-Ag⁺ Interactions Which Induce a Solution Color Change

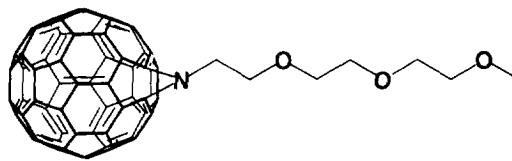
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Abstract: It was found that C₆₀ bearing an NCH₂CH₂(OCH₂CH₂)₂OMe side chain changes its absorption spectrum (and consequently, its visual color) upon addition of AgCF₃SO₃. The spectroscopic studies established that Ag⁺ directly interacts with C = C double bonds on the C₆₀ surface. This system serves as a novel methodology to change spectroscopic and redox properties of C₆₀ by added metal cations. Copyright © 1996 Published by Elsevier Science Ltd

Recently, cation- π interactions have been attracting much attention as a new driving-force for the atom-molecule association.^{1,2} Among them, the Ag⁺- π interaction, which is facilitated by the exceptionally high affinity of Ag⁺ with π -electrons, is the most visualizable and well-characterizable phenomenon.³⁻⁵ Probably, this is why the Ag⁺- π interaction has been studied most extensively so far. Meanwhile, the surface of fullerene homologues is covered with such π -electrons. It is not so easy, however, to gain access to the fullerene surface with non-covalent interactions.⁶ Here, it occurred to us that Ag⁺ might be able to enjoy contact with the electron-rich fullerene surface. If this is the case, this novel interaction is applicable in future to the control of the reactivities, spectroscopic properties, redox potentials, etc. of a fullerene family.

Firstly, we mixed C₆₀ and AgCF₃SO₃ in CHCl₃, but the absorption spectroscopic studies did not show any sign that they interact with each other. We thus used **1**^{7,8} with an oligo(ethylene oxide) chain to retain Ag⁺ near the C₆₀ surface. When the metal salt (solid) was extracted with **1** in chloroform for 30 min under sonication, only



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AgCF₃SO₃ changed the absorption spectrum of **1** (Figure 1A).⁹ The spectral change could be visually followed as a color change from deep orange to reddish orange. Such a color change could not be observed for extraction of solid NaClO₄, Mg(ClO₄)₂, or Zn(ClO₄)₂ salts.

To obtain more quantitative insights into the **1**-metal interaction we measured the absorption spectra in a homogeneous solution (CHCl₃:MeOH = 5:1 v/v). NaClO₄ and Mg(ClO₄)₂ were again ineffective. On the other hand, not only AgCF₃SO₃ but also Zn(ClO₄)₂ could change the absorption spectra although the change induced by Zn(ClO₄)₂ was much smaller than that induced by AgCF₃SO₃ (Figure 1B). From the analysis of A₃₄₀ vs. [salt] plots by the Benesi-Hildebrand equation assuming the formation of a 1:1 complex we estimated the association constants (K_{ass}) to be 180 M⁻¹ (r = 0.99) for Ag⁺ and 90 M⁻¹ (r = 0.96) for Zn²⁺.

Direct evidence for the formation of a 1:1 Ag^+ -**1** complex was also obtained from the measurement of mass spectrum: positive SIMS (2-nitrophenyl octyl ether as a matrix), m/z 881 (M^+), 990 ($[M+\text{Ag}]^+$), where the relative intensity of $[M+\text{Ag}]^+/M^+$ was 1.6 for $[\text{AgCF}_3\text{SO}_3]/[\mathbf{1}] = 5$. On the other hand, the peak assignable to a 2:1 Ag -**1** complex was not detected.

The novel spectral change, particularly observable for Ag^+ , can be rationalized in two different terms: *i. e.*, (i) Ag^+ is entrapped by the interaction with the oligo(ethylene oxide) chain (including that with the nitrogen atom) and the spectral change is due to the inductive effect through the N-C(C_{60}) bond or (ii) Ag^+ is adsorbed onto the C_{60} surface and the spectral change is induced by the direct interaction between Ag^+ and C_{60} . To distinguish between these two effects ^1H NMR spectra of **1** (1.00 mM) were measured in CDCl_3 in the presence of NaClO_4 , AgCF_3SO_3 , and CF_3COOD (50 mM each) (in the case of NaClO_4 the solvent is a mixture of $\text{CDCl}_3:\text{CD}_3\text{OD} = 5:1$ v/v; CD_3OD was used to solubilize NaClO_4). As summarized in Table 1, the ^1H NMR spectrum was not affected by added NaClO_4 , indicating that the $\text{NCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OMe}$ chain is too weak as a ligand to entrap Na^+ . In the presence of CF_3COOD most signals for the methylene protons shifted to lower magnetic field, but the absorption spectrum was not affected. These results mean that D^+ is entrapped only by the oligo(ethylene oxide) chain and does not interact with the C_{60} surface (as in Figure 2A). Furthermore, they provide evidence that the ND^+ scarcely affects the absorption spectrum of the C_{60} moiety through the inductive effect. On the other hand, Ag^+ affected only the δ for the NCH_2 methylene protons to a significant extent. The result, together with the Ag^+ -induced absorption spectral change, supports the view that Ag^+ is entrapped by the N and the C = C double bonds in the C_{60} moiety (as in Figure 2B).¹¹ The foregoing results can be consistently explained as such that "hard" D^+ is favorably bound to "hard" oxygen bases whereas "soft" Ag^+ is favorably bound to "soft" π -electron bases.

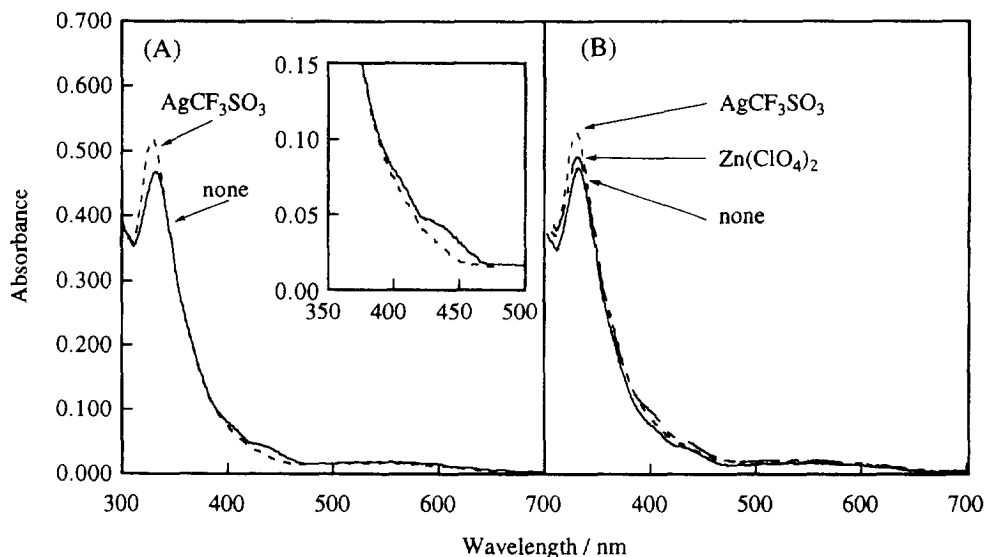


Figure 1. Absorption spectra of (A) **1** (2.00×10^{-5} M) after solid-liquid (CHCl_3) extraction at 25°C and (B) **1** (2.00×10^{-5} M) in the presence of metal salts (50 mM) in a homogeneous $\text{CHCl}_3:\text{MeOH} = 5:1$ v/v solution at 25°C : — none, - - - AgCF_3SO_3 , and - · - · $\text{Zn}(\text{ClO}_4)_2$.

Table 1. $^1\text{H-NMR}$ chemical shift (ppm) induced by M^+ addition in CDCl_3 at 25°C : $[\text{1}] = 5.0 \text{ mM}$, 250MHz .

	a	b	c	d	e	f	g
none	4.06	4.10	3.85	3.75	3.69	3.60	3.40
NaClO_4^a	4.07	4.09	3.87	3.76	3.74	3.62	3.41
	(-0.01) ^b	(-0.01)	(0.00)	(-0.01)	(0.00)	(0.00)	(0.01)
CF_3COOD	4.06	4.16	3.97	3.84	3.80	3.76	3.50
	(0.00) ^b	(+0.06)	(+0.12)	(+0.09)	(+0.11)	(+0.16)	(+0.10)
AgCF_3SO_3	4.36	4.11	3.87	3.79	3.74	3.65	3.39
	(+0.30) ^b	(+0.01)	(+0.02)	(+0.04)	(+0.05)	(+0.05)	(-0.01)

a) The solvent is a mixture of $\text{CDCl}_3:\text{CD}_3\text{OD} = 5:1 \text{ v/v}$; CD_3OD was used to solubilite NaClO_4 . The $\Delta\delta$ values in parentheses are calculated from δ of **1** in $\text{CDCl}_3:\text{CD}_3\text{OD} = 5:1 \text{ v/v}$.

b) The values in parentheses are Chemical shift changes. A plus sign (+) denotes a shift to lower magnetic field, whereas a minus sign (-) denotes a shift to higher magnetic field.

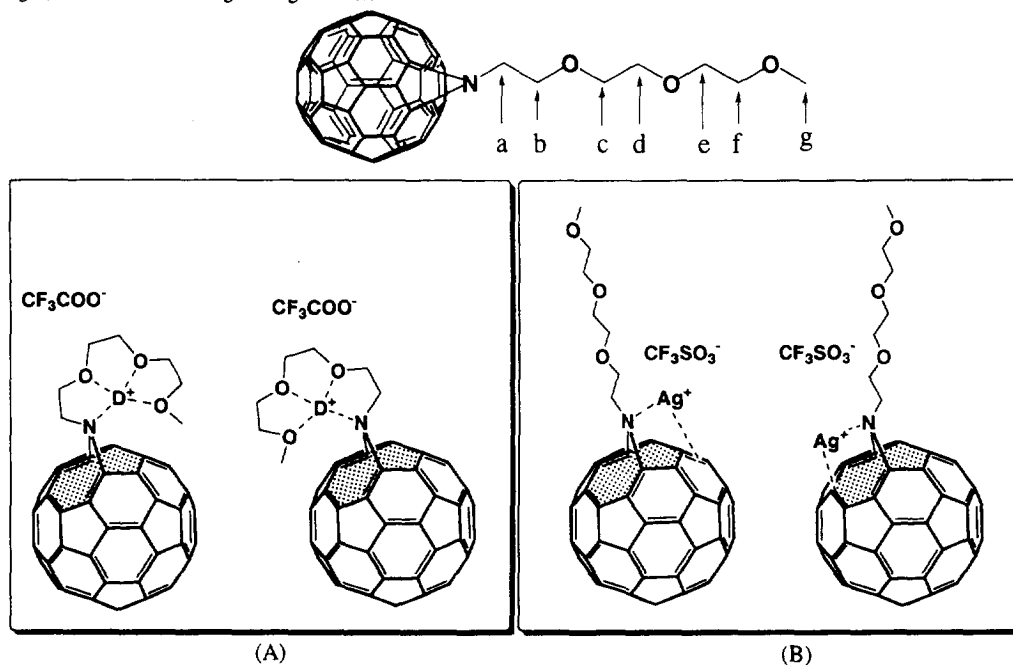


Figure 2. Binding modes for (A) "hard" D^+ and (B) "soft" Ag^+ . In (B) one must take two different binding sites into consideration for the interaction with different $\text{C}=\text{C}$ double bands. (A) may also require two different structures if one takes the direction of lone pair electrons in N into account.

In conclusion, the present paper has shown with firm spectroscopic evidence that Ag^+ , which *a priori* has the peculiar affinity for π -electrons, can interact with the π -electron-rich C_{60} surface with the aid of the 5,6-bridged nitrogen.⁷ To the best of our knowledge, this is the first example that Ag^+ is immobilized near the C_{60}

surface.¹⁰ We believe that the finding and its extended systems are of great importance to reversibly change the spectroscopic and redox properties of C₆₀ and its derivatives by added metal cations.

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9. Metal salts tested herein are LiClO₄, NaClO₄, AgCF₃SO₃, Ca(ClO₄)₂, Zn(ClO₄)₂, and Mg(ClO₄)₂.
10. It is known that a C₆₀ linked with a benzocrown ether at the 6,6-closed position changes its absorption spectrum in the presence of Na⁺, K⁺, Ca²⁺, and Ba²⁺: Osterodt, J.; Nieger, M.; Windscheif, P.-M.; Vögtle, F. *Chem. Ber.*, **1993**, *126*, 2331-2336.
11. The ¹³C NMR spectra of **1** were measured in CDCl₃ in the absence and the presence of AgCF₃SO₃. Although the chemical shifts of several signals were affected by added Ag⁺, this may be due to the direct Ag⁺•••C=C interaction or due to the inductive effect caused by the Ag⁺•••N-C=C interaction. Thus, ¹³C NMR spectroscopy did not give us any useful information about the binding mode.

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