Synthesis of 2-Aminomethylpyridene-appended [60]Fullerenes. On the Difference in the Metal-binding Properties between 5,6-Open and 6,6-Closed Isomers

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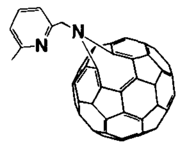
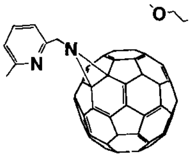
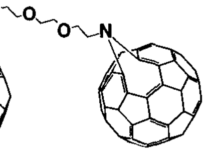
Two 2-aminomethylpyridine-appended [60]fullerenes (**1**) with the 5,6-open and the 6,6-closed structure were synthesized in order to examine the influence of the structural difference on the metal-binding ability. Both compounds could form the 1:1 complex with Ag^+ but the K_{ass} for 5,6-**1** was larger by more than two orders of magnitude than that for 6,6-**1**.

The large availability of [60]fullerene has offered the increasing attention toward exploration of outstanding new physical and chemical properties of this fullerene. Among them, one of the most attractive research objects is the superconductivity observed for certain endohedral [60]fullerene-metal complexes.[1] It occurred to us that the similar phenomenon may emerge not only from such endohedral metal complexes but also from exohedral metal complexes: that is, the metal cation immobilized onto the [60]fullerene surface should facilitate the electron injection into the [60]fullerene moiety and stabilize the $C_{60}^{-}\cdot M^+$ complexes. Such [60]fullerene derivatives with ionophoric functional groups have been synthesized by several groups[2-7] but spectroscopic evidence for the direct [60]fullerene-metal interaction was obtained only in a few systems.[4,7] In this paper, we report a new synthetic method to introduce a 2-aminomethylpyridyl group into [60]fullerene with a 5,6-open and a 6,6-closed linkage (5,6-**1** and 6,6-**1**, respectively) and examine the difference in their metal-binding properties. To the best of our knowledge, this work is the first example that the metal complexation behaviour appeared so differently between 5,6-open and 6,6-closed isomers[8] and therefore has an important implication in molecular design of ionophoric [60]fullerenes.


5,6-**1**


6,6-**1**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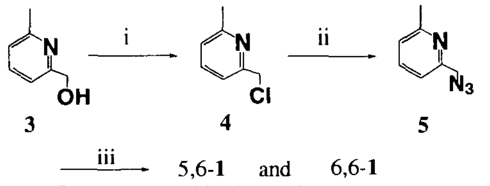
Compounds 5,6-**1** and 6,6-**1** were synthesized from 2-methyl-6-hydroxymethylpyridine (**3**) via its azide derivative (**5**) according to Scheme 1. 5,6-**1** and 6,6-**1** were isolated by flash column chromatography (silica gel, toluene:hexane = 1:1 v/v) and identified by ^1H NMR, ^{13}C NMR, and Mass (positive SIMS: m/z 840 (M^+)) spectral evidence and elemental analyses. In ^{13}C NMR spectroscopy the fullerene moiety of 5,6-**1** has 32 peaks at sp^2-hybridized carbon region (110-150 ppm), supporting the 5,6-open structure with C_s symmetry whereas that of 6,6-**1** has 15 peaks at sp^2-hybridized carbon region and one peak (84.68 ppm) at sp^3-hybridized carbon region, supporting the 6,6-closed structure with C_{2v} symmetry. Furthermore, in the absorption spectroscopy of 6,6-**1** a new absorption band appeared at 423 nm, which is a characteristic of the 6,6-closed structure.[8] These lines of spectroscopic evidence are consistent with the structures of 5,6-**1** and 6,6-**1**.



Scheme 1. Reagents (yield): i, $SOCl_2$ in benzene (84%); ii, NaN_3 in DMF (not isolated; one spot on TLC); iii, [60]fullerene, reflux in toluene (5% both for 5,6-**1** and 6,6-**1** based on consumed [60]fullerene).

Both compounds are soluble in 1,1,2,2-tetrachloroethane (TCE) and toluene, but 5,6-**1** is more soluble in TCE than 6,6-**1** whereas 6,6-**1** is more soluble in toluene than 5,6-**1**. The solubility difference suggests that 5,6-**1** bearing an amino group conjugated with the [60]fulleroid π-system is more polar than 6,6-**1** bearing an amino group insulated by a sp^3-carbon from the [60]fullerene π-system.

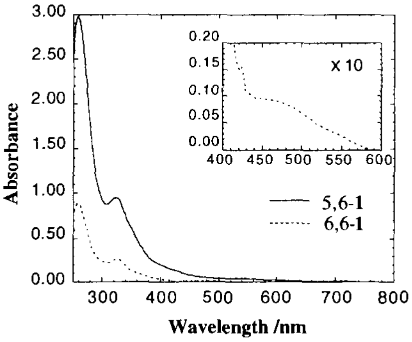


Figure 1. Absorption spectra of 5,6-**1** and 6,6-**1** (2.00×10^{-5} mol dm^{-3}) in toluene:methanol (19:1 v/v) at 25 °C.

In order to dissolve metal salts we chose a toluene: methanol (= 19:1 v/v) mixture as a standard solvent.[9] As shown in Figure 1, the absorption spectra were somewhat different between azafulleroid 5,6-**1** with λ_{max} 258 nm ($\varepsilon = 1.5 \times 10^5$) and 323 nm ($\varepsilon = 4.7 \times 10^4$) and azafullerene 6,6-**1** with λ_{max} 258 nm ($\varepsilon = 4.5 \times 10^4$) and 326 nm ($\varepsilon = 1.3 \times 10^4$). The absorption spectra were scarcely changed by the addition of CF_3COOH (as a proton source) and $NaClO_4$ whereas they were significantly changed by the addition of CF_3SO_3Ag (Figure 2). These results indicate that Ag^+ interacts primarily with the amine ligands and additionally with the C=C double bonds.[7,10]

To obtain an insight into the stoichiometry of the Ag^+ complexes we carried out ^1H NMR mesurements to make Job plots.[11] In a toluene-d_8:methanol-d_4 (19:1 v/v) mixture at 25 °C

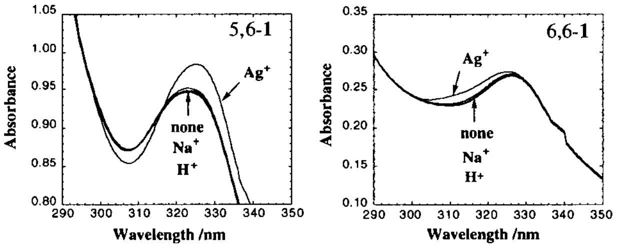


Figure 2. Absorption spectral change of **5,6-1** and **6,6-1** (2.00 × 10^{-5} mol dm^{-3}) in the presence of CF_3SO_3Ag, $NaClO_4$, and CF_3COOH (2.00 × 10^{-2} mol dm^{-3}).

a large chemical shift change was observed for the NCH_2 and the CH_3 protons. Strangely, in the presence of 0.10 mol dm^{-3} CF_3SO_3Ag the NCH_2 and the CH_3 protons in **5,6-1** (1.00 × 10^{-3} mol dm^{-3}) moved to lower magnetic field (0.02 and 0.13 ppm, respectively) whereas those in **6,6-1** (1.00 × 10^{-3} mol dm^{-3}) moved to higher magnetic field (0.08 and 0.84 ppm, respectively). The unusual up-field shift in **6,6-1** is rationalized as such that the conformational change in the ligand moiety is induced by the Ag$^+$-binding and the protons are affected by the anisotropic effect of the fullerene π-system.

The Job plots ([**5,6-1** or **6,6-1**] + [CF_3SO_3Ag] = 1.00 × 10^{-3} mol dm^{-3} (constant)) of the chemical shifts gave a break-point at 0.5, indicating that both **5,6-1** and **6,6-1** form a 1:1 complex with Ag$^+$. The mass spectral data (positive SIMS, matrix *o*-nitrophenyl octyl ether) also support this view: when **1** and CF_3SO_3Ag were mixed in a 1:1 or 1:5 molar ratio, only the peak for [**1** + Ag]$^+$ was observed at 948.8. When CF_3SO_3Ag was replaced with $NaClO_4$, the peak for [**1** + Na]$^+$ was not observed.

Based on the foregoing results, we estimated the association constants (K_{ass}) for the 1:1 complex by an absorption spectroscopic method. As shown in Figure 3, a much larger spectral change was observed for **5,6-1** and the K_{ass} for **5,6-1** (1.2 × 10^6 dm^3 mol^{-1}) was also much larger than that for **6,6-1** (2.5 × 10^3 dm^3 mol^{-1}) (in toluene:methanol = 19:1 v/v). Under the similar conditions (in TCE:methanol = 19:1 v/v; **2**[12] is not so soluble in toluene:methanol = 19:1 v/v), compound **2** bearing the 5,6-open structure and only one amino group gave the K_{ass} = 4.4 × 10^3 dm^3 mol^{-1}. This value is smaller than the K_{ass} for **5,6-1** (9.3 × 10^5 dm^3 mol^{-1} in TCE:methanol = 19:1 v/v), indicating that the pyridine nitrogen in **5,6-1** also contributes to the Ag$^+$-binding.

In conclusion, the present paper demonstrated for the first time the influence of the structural difference between "5,6-open" and "6,6-closed" on the metal-binding properties. The larger K_{ass} and the larger spectral change induced for **5,6-1** indicate that an amino group conjugated with the [60]fulleroid π-system more strongly interacts with Ag$^+$ than that insulated from the [60]fullerene π-system. We believe that the remarkable difference between these two structures are very important to design the [60]fullerene-containing ligands, particularly, those which expect the metal-π interaction on the fullerene surface.

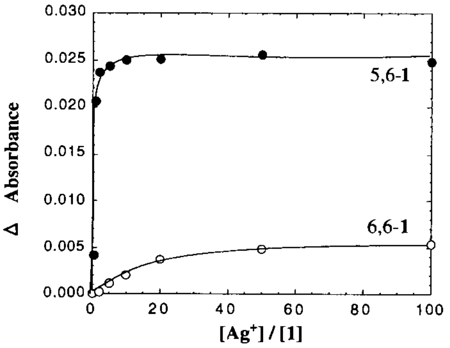


Figure 3. Absorption spectral change at 323 nm for **5,6-1** and 311 nm for **6,6-1** : [**1**] = 2.00 × 10^{-5} mol dm^{-3}.

References and Notes

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8 For the synthesis and structure determination of 5,6-open and 6,6-closed isomers see J. Averdung and J. Mattay, *Tetrahedron*, **52**, 5407 (1996) and references cited therein.
9 We found that the absorption spectra of **5,6-1** in toluene are slightly changed by the addition of a trace amount of methanol, but they are scarcely changed at 0.5 ~ 5.0 vol%.
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11 600 MHz, 25 °C, toluene-d_8:methanol-d_4 = 19:1 v/v.The δ_H of NCH_2 and CH_3 of **5,6-1** are 5.09 and 2.52 ppm, and those of **6,6-1** are 4.08 and 2.44 ppm, respectively.
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