

## **THERMAL MODIFICATION OF FERROCENE DERIVATIVE ADDUCTS TO C<sub>60</sub> FOR STM OBSERVATIONS**

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### **Abstract**

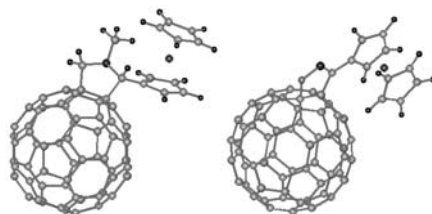
Molecules that may adopt various stable conformations might be applied to store information. The conformational changes could be induced by suitable polarized tip of STM. For the STM experiments two types of fullerene:ferrocene cycloadducts (C<sub>60</sub>:Fn) were selected where ferrocene fragment is bound to C<sub>60</sub> at the 6-6 bond by different heterocyclic pentagon rings. According to semiempirical quantum chemistry calculation one of them may be used to STM observation without any modification, while the second cycloadduct must be exposed to thermal treatment in order to obtain bistable molecule.

**Keywords:** different conformations, fullerene:ferrocene cycloadduct, STM investigation, thermal modification

### **Introduction**

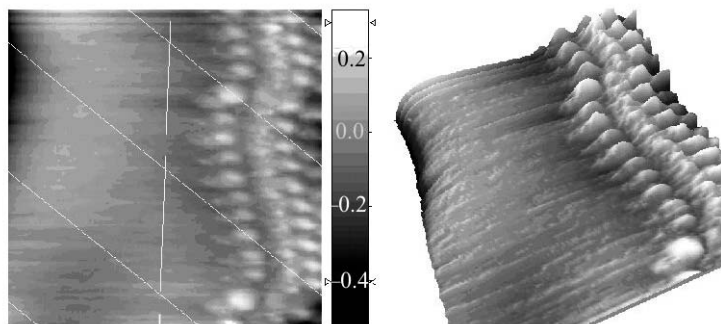
High capacity of data stored in small-size devices is looked for in recent information technology. It was announced recently that the 64-bit memory chip based on molecular switches was built at Hewlett-Packard; in the chip single bit was written on approx. 1000 molecules [1]. However individual molecules or assembly of molecules may be utilized for the purpose, e.g. Tomanek *et al.* [2] proposed a memory unit consisting of carbon nanocapsule C<sub>480</sub> and endohedral fullerene K@C<sub>60</sub>, that could be shifted between two ends inside the capsule by external electric field. Memory devices were also built from polymers using the spin-crossover phenomenon [3]. Any molecule that may adopt different stable conformations with comparable binding energy could be used to store information if the potential barrier separating the two states is high enough to prevent spontaneous transition between them yet enough low to make possible change of the conformation under the external influence. The change of conformation e.g. rotation of the active fragment of the molecule might be induced by external electric field generated by polarized tip of scanning tunneling mi-

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**Fig. 1** The structure of the two fullerene-ferrocene adducts in perpendicular ( $C_{60}CH_2NCH_3CHF_n$ , **1**) and parallel conformation ( $C_{60}ONCF_n$ , **2**)

roscope (STM) in process of writing information or determined by the STM to read information. Molecules for the STM experiments ought to have high density of electronic states because imaging by the method relies on tunneling of electrons between the STM tip and the investigated object. Fullerenes are particularly suitable for such experiments because of high density of states and because they may carry various functional groups. For the STM experiments two types of fullerene:ferrocene ( $C_{60}:Fn$ ) cycloadducts were selected, where ferrocenyl group ( $C_5H_4FeC_5H_5$ ) is bound to fullerene by various heterocyclic rings:  $C_{60}C(H_2)N(CH_3)CHF_n$  (**1**, N-methyl-2-ferrocenyl-3,4-fulleropyrrolidine) and  $C_{60}ONCF_n$  (**2**) (Fig. 1). The compounds  $C_{60}CH_2NCH_3CHF_n$  and  $C_{60}ONCF_n$  were synthesized according to the procedures described in [4] and [5, 6], respectively. Preliminary STM measurements proved that the  $C_{60}:Fn$  complexes might be well imaged using the STM/UHV microscope. The  $C_{60}ONCF_n$  compound dissolved in dichloroethane  $C_2H_4Cl_2$  was deposited on freshly cleaved (0001) basal plane of highly oriented pyrolytic graphite. The complexes form linear chains with the ferrocene group protruding at one side (Fig. 2).



**Fig. 2** 2-D statement image of  $20 \times 20 \text{ nm}^2$  area of HOPG with chains of  $C_{60}ONCF_n$  complexes, large bright spots are interpreted as  $C_{60}$  and the smaller objects attached at the left side as the adducted Fn groups (left). The gray scale indicates height of the structure. 3-D STM statement image of area (right)

According to the semiempirical quantum chemical calculation based on the Neglect of Diatomic Differential Overlap approximation with PM3 parameterization [7] the cyclopentadienyl  $C_5H_5$  and heterocyclic  $-CCNOC-$  ring in the molecules may be

either parallel or perpendicular to each other with the same heat of formation. Thus the Fn fragment might rotate around single bond between cyclopentadienyl and heterocyclic attached to  $C_{60}$  rings if the potential barrier at intermediate states was not too high. Free rotation of the Fn group in complex (2) is blocked only by  $\pi$ -bond while in (1) complex by  $CH_3$  group.

The calculations proved also that the electric dipole moment induced by the external electric field may cause rotation of the Fn group in complex (2) though not in the other one. However the potential barrier preventing rotation may be modified by thermal decomposition of the complex if condition to free  $CH_3$  were found. Here are presented results of thermal analyses of the complex (1) by thermogravimetry (TG) and differential scanning calorimetry (DSC) and identification of the products by the  $^1H$  NMR method.

## Experimental results and discussion

Thermal decomposition of the  $C_{60}ONCFn$  compound described in [8] occurs as a single step exothermic process in the temperature range 300–450°C. In this temperature range bonds between  $C_{60}$  and heteroatom ring and ferrocene break leaving atomically dispersed iron in the fulleride lattice. Those experiments helped to determine annealing temperature range and interpret DSC and TG plots observed during annealing  $C_{60}CH_2NCH_3CHF_n$  compound.

The experiments on thermally induced partial decomposition of the complex (1) (Fig. 3) were carried out using DSC and TG methods with a DuPont Instruments. The measurements were performed at  $10^\circ C\ min^{-1}$  heating rate under helium atmosphere with the flow rate of  $25\ mL\ min^{-1}$ .

The fresh sample loses up to 10 mass% in the temperature range 280–300°C. The mass loss ought to be ascribed to residual toluene. The sample remained soluble in organic solvents and  $^1H$  NMR spectrum was identical as observed in the fresh one. The adduct begins to decompose at 305°C, it proceeds as a three-step process (Fig. 3). The first step extends to  $\sim 370^\circ C$  with the mass loss of 2 mass% relatively to the molecular

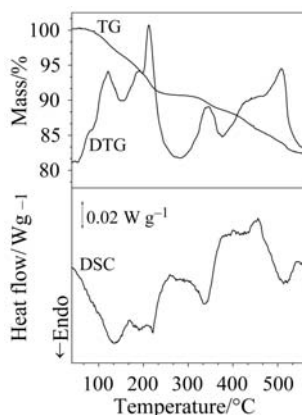


Fig. 3 DSC and TG results on  $C_{60}CH_2NCH_3CHF_n$  powder

mass of the complex. The next step occurs in the range of 370–450°C followed by process in the temperature range 450–550°C. Each of the processes is connected with approximately 3 mass% mass loss. The total mass loss proves that annealing even up to 550°C is insufficient to remove all organic groups from the C<sub>60</sub> based complex.

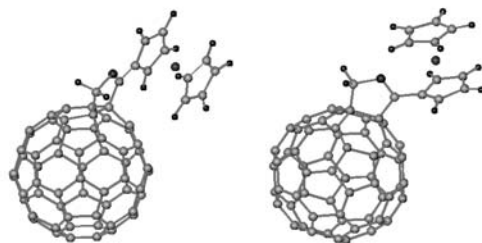
The only fragment that could be released with a mass loss close to 2 mass% at 370°C is the methyl group, probably with additional hydrogen atom from CH or CH<sub>2</sub> fragment that amounts to 1.7 mass% of molecular mass. According to the theoretical calculation freeing methane CH<sub>4</sub> requires similar energy of ~10–12 kcal mol<sup>-1</sup> in both cases. Because of similar probability of both processes, it has to be assumed that the annealed sample contains two species: **a)** C<sub>60</sub>C(H<sub>2</sub>)NCC<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub> and **b)** C<sub>60</sub>CHNCHC<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>.

The <sup>1</sup>H NMR spectrum is compatible with the notion that the methyl group is freed at elevated temperatures. The experimental <sup>1</sup>H NMR line positions in fresh sample and in annealed to 370°C and interpretation of the lines are listed in Table 1.

**Table 1** Comparison of <sup>1</sup>H NMR in C<sub>60</sub>C(H<sub>2</sub>)N(CH<sub>3</sub>)CHC<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub> and C<sub>60</sub>C(H<sub>n</sub>)NCH<sub>m</sub>C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>, where *n*=1, 2; *m*=1, 0; (200 MHz; solvent: CS<sub>2</sub>/CDCl<sub>3</sub>=2/1)

Assignment	C <sub>60</sub> CH <sub>2</sub> NCH <sub>3</sub> CHC <sub>5</sub> H <sub>4</sub> FeC <sub>5</sub> H <sub>5</sub>	C <sub>60</sub> CH <sub>n</sub> NCH <sub>m</sub> C <sub>5</sub> H <sub>4</sub> FeC <sub>5</sub> H <sub>5</sub>	Type
	δ / ppm	δ / ppm	
CH <sub>3</sub>	3.44	–	singlet
CH <sub>2</sub>	4.27, <i>J</i> =9.4 Hz	4.02	doublet
C <sub>5</sub> H <sub>5</sub>	4.31	4.04	singlet
C <sub>5</sub> H <sub>4</sub>	4.21	3.68	multiplet
C <sub>5</sub> H <sub>4</sub>	4.26	3.97	multiplet
C <sub>5</sub> H <sub>4</sub>	4.49	4.12	multiplet
C <sub>5</sub> H <sub>4</sub>	4.58	4.17	multiplet
CH	4.83	4.33	singlet
CH <sub>2</sub>	4.89, <i>J</i> =9.4 Hz	4.56	doublet

Only one of the two possible complexes C<sub>60</sub>CH<sub>2</sub>NCFn (**a**) may adopt two different conformations. In the first conformation, the cyclopentadienyl C<sub>5</sub>H<sub>5</sub> and heterocyclic –C(H<sub>2</sub>)NCC– rings are parallel and in second one the rings are perpendicular (Fig. 4).



**Fig. 4** Two possible conformations of the C<sub>60</sub>CH<sub>2</sub>NCFn (**a**) adduct formed by thermal modification of the C<sub>60</sub>CH<sub>2</sub>NCH<sub>3</sub>CHF<sub>n</sub> complex

The calculations of the  $C_{60}CH_2NCFn$  complex in uniform external electric field proved possibility of changing externally structure of molecule by the electric field. The calculations were repeated for gradually increasing electric field until the Fn group rotated to such an angle that it relaxed to another conformation than the initial one with the electric field switched off. To induce the rotation electric field of intensity  $\sim 3 \text{ V nm}^{-1}$  oriented almost perpendicular to the  $C_5H_5$  ring is required. The transitions between parallel and perpendicular positions of  $C_5H_5$  and  $CNCH_2C_{60}$  rings are reversible.

## Conclusions

Fullerene:ferrocene complex (**1**) may be thermally modified to the form that exists in two conformations sensitive to the external electric field. The molecules on HOPG substrate may be relatively easy imaged with the STM method and ferrocene groups are clearly visible. The complexes are arranged in long straight chains and do not move during the STM experiments. Yet it was neither possible in our experiments to distinguish conformation of adducted Fn groups nor modify conformation with the STM tip.

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