Journal of Chromatography A, 1323 (2014) 174–178

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Short communication

Development of a C_{60}-fullerene bonded open-tubular capillary using a photo/thermal active agent for liquid chromatographic separations by π–π interactions

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ARTICLE INFO

Article history:
Received 30 July 2013
Received in revised form 30 October 2013
Accepted 31 October 2013
Available online 11 November 2013

Keywords:
C_{60}-fullerene
Perfluorophenyl azide
Liquid chromatography
π–π interaction
Polycyclic aromatic hydrocarbons

ABSTRACT

This short communication describes a newly developed open-tubular capillary which was coated with C_{60}-fullerene by a covalent bonding via a photo/thermal active agent. We utilized perfluorophenyl azide (PFPA) as an active agent, which can be used for the "photo click" coupling of the carbon materials. The inner wall of a fused silica capillary was treated with silane conjugated PFPA, and then C_{60}-fullerene was chemically modified by a photoreaction or a thermal reaction. Through evaluations of the capillaries by liquid chromatography, the separation characteristics of three polycyclic aromatic hydrocarbons (PAHs) were confirmed in both capillaries. With comparison of the retention behavior to a commonly used C_{18} column, the prepared capillaries showed the specific separation ability based on the π–π stacking by C_{60}-fullerene. The capillary prepared by the thermal reaction provided the base line separation of phenanthrene, triphenylene, and benz[a]pyrene within 3 min at 18.8 cm capillary length.

1. Introduction

Carbon nano-materials such as a fullerene, graphene, and nanotube have been widely studied in the fields of semiconductors, conductive transparent films, medicines, etc. because of their excellent thermal and/or electrical conductivity, physical strength, and specific surface area [1–4]. These carbon materials consist of a π-conjugated system from sp^2 carbons and π electrons that are diffusely distributed within the molecule. The π electrons provide the dipole interaction based on the London dispersion force and allow the π–π interaction in regard to the aromatic compounds. According to the specific interaction, the carbon nano-materials have been applied for the separation media in liquid chromatography (LC), capillary electrochromatography (CEC), capillary electrophoresis, and solid phase extraction [5–11]. In common cases of these applications, the introduction of the various functional groups to the surface of the carbon materials was necessary for the immobilization onto the substrate or improvement of solubility/dispersibility. However, the introduction of the functional groups provided opportunity for other interactions, such as hydrogen bonding and ionic interaction. Therefore, in order to obtain the separation medium having characteristic π–π interactions, another technique is required to immobilize the carbon materials.

Perfluorophenylazide (PFPA) is a photo/thermal active molecule for the conjugation of carbon materials, polymers, and carbonhydrates [12–16], PFPA is effective for reaction with the conjugated double bond because of the occupied fluorine atoms, therefore the unexpected reactions such as a dimerization and cyclization via the azide-based molecules occur less frequently [17,18]. We also previously reported the effective immobilization of the graphene flakes, alkyl chain-modified nanoparticles, polymer thin films, and small molecules by the PFPA derivatives [19,20]. The aim of this study is to achieve simple yet effective preparation of the carbon-based separation medium via the PFPA derivatives. A fused silica capillary modified with C_{60}-fullerene, which has higher solubility/dispersibility compared to the other carbon nano-materials and suitable reactivity based on its spherical morphology [21–23], was evaluated by capillary LC. We examined the effects against the retention behavior by C_{60}-fullerene and achievement of selective separations of several polycyclic aromatic hydrocarbons (PAHs) by the π–π interaction. In this communication, we propose a simple and effective method for the preparation of the C_{60}-fullerene immobilized separation medium.

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http://dx.doi.org/10.1016/j.chroma.2013.10.097

Table 1
Contents of the prepared capillaries.

	Step 1	Step 2
Capillary-A	PFPA-silane/methanol	Methanol without C_{60} (UV)
Capillary-B	PFPA-silane/methanol	Toluene without C_{60} (UV)
Capillary-C	PFPA-silane + C_{60}/toluene (UV)	C_{60}-PFPA-silane/toluene (silane coupling)
Capillary-D	PFPA-silane/methanol	C_{60}/toluene (UV)
Capillary-D′	PFPA-silane/methanol	C_{60}/toluene (UV)
Capillary-E	PFPA-silane/methanol → Filling C_{60}/toluene and dry (3×) → Thermal reaction (no UV)	

Capillaries-A, -B, UV irradiation with only the solvent in capillary; Capillary-C, synthesis of PFPA conjugated C_{60}-fullerene and silane coupling in the capillary at 2nd step; Capillary-D, following as Fig. 1; Capillary-E, by thermal reaction without any UV reactions. Column size, Capillary-A, -B, -C, -D, 50 μm i.d.; Capillary-D′, -E, 25 μm i.d.

2. Experimental

2.1. Chemicals and instruments

Deionized water was obtained from Milli-Q (Direct-Q 3UV) and all solvents were purchased from Wako Chemicals (Osaka, Japan). C_{60}-fullerene was purchased from SES Research (Huston, TX, USA). The other reagents for the solutes in LC, the synthesis of PFPA derivatives, and the mobile phases were purchased from Nacalai Tesque (Kyoto, Japan). A fused-silica capillary (25 μm i.d., 375 μm o.d.) was purchased from Polymicro Technologies (Phoenix, AZ, USA). A transparent fused-silica capillary (25 μm i.d.) was purchased from GL Science (Tokyo, Japan).

Capillary LC experiments were performed with a P/ACE MDQ system (Beckman Coulter, Fullerton, CA, USA) equipped with a UV absorbance detector. For Fourier transform infrared spectroscopy (FTIR), a Nicolet iS5 FT-IR (ThermoScientific, Waltham, MA, USA) was used for the definition of the synthesized compounds.

2.2. Preparation of a C_{60}-fullerene bonded capillary

N-(3-trimethoxysilylpropyl)-4-azido-2,3,5,6-tetrafluorobenzamide (PFPA-silane) was synthesized according to the previous studies [24,25]. The synthesis procedures including the scheme and FT-IR spectra of products are summarized in Supplementary data (Scheme S1, Fig. S1). All the capillaries were washed with 1.0 M HCl aq., 1.0 M NaOH aq., and water to activate silanol groups of capillary inner wall. After drying with N_2 purge, PFPA-silane solution in methanol (12.6 mM) was passed through the Capillary-A, -B, -D, and -E at 10 μL/h for 24 h. Then, methanol, toluene, and C_{60}-fullerene in toluene (36 mM) were filled in Capillary-A, -B, and -D, respectively.

For Capillary-C, PFPA-silane in toluene (12.6 mM) and C_{60}-fullerene in toluene (36 mM) were mixed and treated by UV irradiation for 20 min in advance. The mixture was filled into the activated capillary. The capillary was folded for 24 h in ambient.

Additionally, in order to obtain a capillary which was modified with C_{60}-fullerene at higher density, the thermal reaction was employed for the immobilization of C_{60}-fullerene instead of UV irradiation. As shown in Table 1, Capillary-D′ was prepared by the same method as Capillary-D except with a smaller diameter. For Capillary-E, C_{60}-fullerene saturated in toluene was filled into the activated capillary (25 μm i.d.) and dried under vacuum to evaporate the solvent (3×). The capillary was treated at 170 °C for 5 h. Then, dichlorobenzene was filled into the capillary and treated by sonication for 5 min to remove the unreacted C_{60}-fullerene.

After each reaction, all the capillaries were washed with dichloromethane and methanol by pump to remove the unreacted C_{60}-fullerene. The reaction schematic for Capillary-D is shown in Fig. 1. Also, the preparation conditions of all the capillaries are summarized shown in Table 1.

The LC evaluations were carried out under the following conditions: capillary size, 50 μm i.d. or 25 μm i.d. mobile phase, water/acetonitrile or water/methanol/tetrahydrofran (THF); pressure, 50 mbar; injection, 50 mbar – 3 s; detection, UV 200 or 254 nm; temperature, 25 °C. Other conditions are listed in each figure caption. The retention factor is defined as follows:

$$\text{Retention factor,}\quad k = \frac{t_R - t_0}{t_0},$$

t_R: retention time of solute, t_0: retention time of acetone.

3. Results and discussion

3.1. Effect of the modification with C_{60}-fullerene

To examine the effect of the modification with C_{60}-fullerene, Capillaries-A to -D were evaluated by capillary LC using acetone and benzene as solutes. The chromatograms in each capillary are shown in Fig. 2. From these results, only Capillary-D allowed separation ability of the two solutes. Both of Capillary A and B were prepared without C_{60}-fullerene, so that we confirmed the solvents did not affect the retention of benzene. Regarding Capillary-C, we tried to synthesize the C_{60}-fullerene attached PFPA-silane by direct silane coupling to capillary inner wall. However, the specific retention based on C_{60}-fullerene was not observed. We assumed that the reaction between C_{60}-fullerene and PFPA was not complete, so that the retention property of the capillary was similar to Capillary-B. On the other hand, the base-line separation of acetone and benzene was achieved in Capillary-D. The result suggests bonding of C_{60}-fullerene under these conditions.

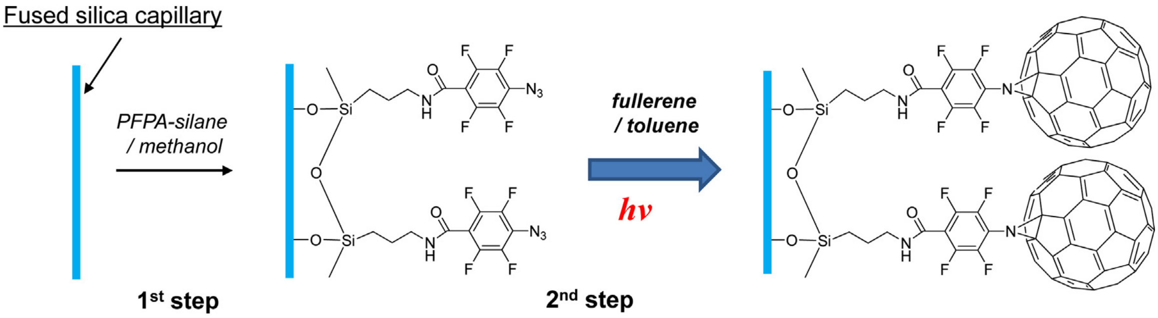

Fig. 1. Schematic image of the preparation of the C_{60}-fullerene bonded capillary.