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Features of a truxene-based stationary phase in capillary gas chromatography for separation of some challenging isomers

Qing Lv[a,b], Shuai Feng[c], Lingmin Jing[a], Qing Zhang[b], Meiling Qi[a,*], Jinliang Wang[a,*], Hua Bai[b], Ruonong Fu[a]

[a] Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials and School of Chemistry, Beijing Institute of Technology, Beijing 100081, China
[b] Institute of Industrial and Consumer Product Safety, Chinese Academy of Inspection and Quarantine, Beijing 100176, China
[c] College of Chemistry and Chemical Engineering, Taishan University, Taian 271021, China

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ABSTRACT

Herein we report the first example of exploring truxene-based derivatives for gas chromatographic (GC) separations. The fabricated thiophene-functionalized truxene (TFT) column exhibited weak polarity and efficiencies as high as 4000 plates/m for 0.250 mm i.d. columns. TFT column showed preferential retention for halogenated and alkyl benzene analytes, and especially, high resolving capability for the xylene isomers, di- and trichlorobiphenyls (di-CB and tri-CB) isomers. Interestingly, its unique retentions for the latter analytes were found to be closely related with their dihedral angles and the locations of chlorine atoms. This finding on the retention trend has not been reported in GC separations, which may provide a new perspective in elucidating retention behaviours for specific analytes. Moreover, TFT column exhibited high thermal stability up to 320 °C and excellent repeatability. This work demonstrates the promising future of truxene derivatives in the separation science.

1. Introduction

Truxene (Fig. 1, left) is a rigid planar heptacyclic polyarene with a Y-shape structure [1,2], and can easily be functionalized in three diverging directions in space to serve as an excellent building block for constructing star-shaped oligomers and dendritic materials [3]. In the past decades, truxene derivatives have gained growing attention in the areas of polyarenes and fullerenes [4], liquid crystals [5,6], photoelectric materials [7,8] and sensors [9,10]. Many truxene derivatives exhibit fascinating characteristics such as nanosized planar π-conjugated structures with large diversity in architectures, high thermal stability and good solubility in common organic solvents, which render them attractive as advanced chromatographic separation media. Unfortunately, their potential in separation science remains unexplored, to the best of our knowledge.

Selective separation of challenging isomers, such as xylene isomers and polychlorobiphenyl (PCB) isomers, is of vital importance in chemical industries and environmental analysis. Capillary gas chromatography (GC) is one of the most efficient separation methods for the task. However, baseline resolution of *p*-xylene from *m*-xylene is still one of the tough issues due to their extremely high resemblance of physical properties [11,12]. Only few stationary phases available could fulfill the demanding task for the separation *p*-/*m*-xylene [13–16]. PCBs are classified as persistent organic pollutants and banned in many countries, but they are difficult to be well separated, especially those isomers with the same chlorine atoms [17]. Accordingly, developing highly selective GC stationary phases has been the pursuit of the researchers in chromatography [18–21].

In this study, we report a thiophene-functionalized truxene derivative (TFT, Fig. 1, right) as new type of stationary phases for gas chromatographic (GC) separations. TFT has an extended π-conjugated structure by the three thiophene units and good solubility in organic solvents facilitated by its six hexyls. After it was statically coated on a fused-silica capillary column, its column efficiency, polarity, separation performance, column repeatability and thermal stability were investigated. In addition, two commercial columns, HP-5MS (5% phenyl methylpolysiloxane) and DB-35 (35% phenyl methylpolysiloxane), were employed for reference.

* Corresponding authors.
E-mail addresses: mlqi@bit.edu.cn (M. Qi), jinlwang@bit.edu.cn (J. Wang).

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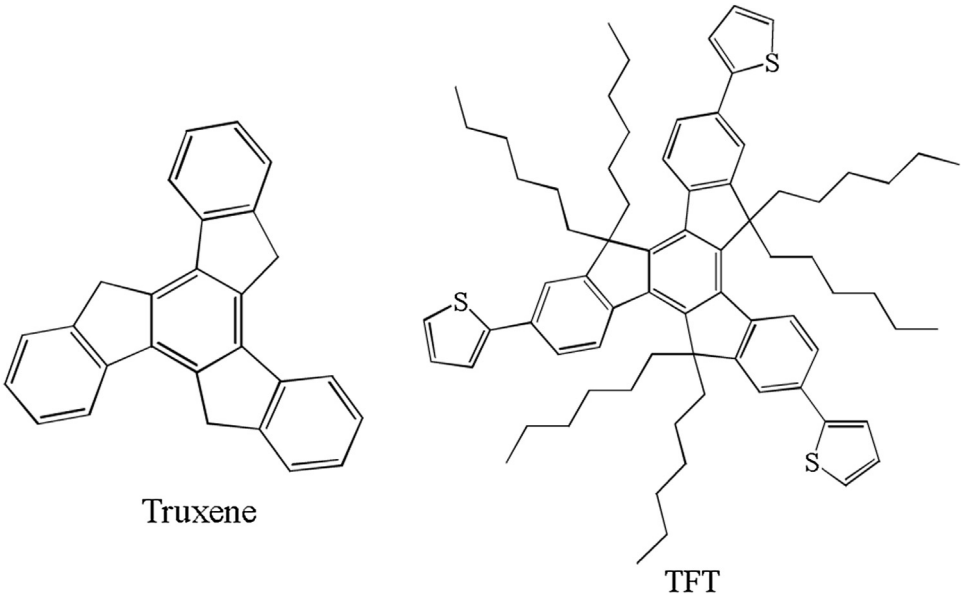

Fig 1. Structures of truxene and TFT.

2. Experimental

2.1. Materials and instruments

TFT was synthesized according to the method of our previous reports [22,23]. The PCBs used in this study were standard reagents purchased from AccuStandard Inc. (New Haven, CT, USA). Other analytes were at least of analytical grade. Untreated fused-silica capillary (0.25 mm, i.d.) was purchased from Yongnian Ruifeng Chromatogram Apparatus Co., Ltd. (Hebei, China). The commercial HP-5MS and DB-35 capillary columns (10 m long × 0.25 mm, i.d., 0.25 μm film thickness) were purchased from Agilent Technologies.

An Agilent 6890 gas chromatograph (Agilent Technologies, USA) equipped with a split/splitless injector, a flame ionization detector (FID) and ChemStation software was used. All the GC separations were performed under the following conditions: nitrogen of high purity (99.999%) as carrier gas; injection port at 250 °C; split ratio of 30:1; FID at 250 °C. A Mettler TGA/DSC1 thermal gravimetric analyzer (Zurich, Switzerland) was employed for determination of thermal stability of TFT stationary phase, which was performed from 30 °C to 600 °C at a ramp rate of 10 °C/min under nitrogen. The scanning electron microscopy (SEM) micrographs were recorded on a Hitachi S4800 microscope (Tokyo, Japan).

2.2. Preparation of TFT-coated capillary column

A fused-silica capillary column (10 m × 0.25 mm, i. d.) was purged with nitrogen at 200 °C for 3 h and pretreated with a saturated solution of sodium chloride in methanol for capillary inner surface roughing to facilitate the uniform coating of a stationary phase on the capillary inner wall. The pretreatment process was performed as follows. Briefly, a suspension of sodium chloride, which was obtained under stirring condition by addition of 6 mL of saturated solution of sodium chloride in methanol into 16 mL of trichloromethane, passed through the capillary column. After the liquid was expelled from the column, the column stayed at 200 °C for 3 h under nitrogen atmosphere. After the pretreatment, the capillary column was statically coated with the solution of TFT stationary phase in dichloromethane (0.25%, w/v) at 39 °C. During the coating process, one end of the capillary column was sealed and the other end was connected to a vacuum system to gradually remove the solvent under vacuum. The coated capillary column was then conditioned from 40 °C to 200 °C at the rate of 2 °C/min and held at the high-end temperature for 6 h under nitrogen at 1.0 mL/min.

Table 1
McReynolds constants of the TFT and commercial columns under 120 °C.

Column	X′	Y′	Z′	U′	S′	General polarity
TFT	78	143	125	78	155	579
HP-5MS	30	72	62	96	65	325
DB-35	102	142	145	219	178	786

The elution sequence of the probes on TFT column was 1-butanol, benzene, 2-pentanone, 1-nitropropane and pyridine. X′ represents benzene for the π-electron and dispersive interactions; Y′ refers to 1-butanol for probing the hydrogen-bonding ability of the phase; Z′ refers to 2-pentanone for the polarizability and dipolar interactions; U′ represents nitropropane related to the dipole interactions; and S′ refers to pyridine, a strong proton acceptor that detects the acidic character of the phase.

3. Results and discussion

3.1. Characterization of TFT stationary phase and capillary column

Thermogravimetric analysis (Fig. 2a) indicates that TFT is thermally stable up to 390 °C where 5% weight loss can be observed, suggesting its potential as GC stationary phase. From Fig. 2b, it can be seen that the fabricated TFT column exhibited high column efficiency of 4016 plates/m at 0.6 mL/min. At the rates above 0.7 mL/min, it showed higher column efficiencies than the two commercial columns. It should be noted that the column efficiency of TFT stationary phase is considerably high in view of its solid form on the capillary inner wall. Figs. 2c and 2d present the SEM images of the cross sections of the as-fabricated column, showing its coating thickness of approximately 100 nm on the capillary inner wall.

Column polarity is an important chromatographic parameter for GC column evaluation and selection in practical use. Usually, it is evaluated by the general polarity obtained by summing up of the determined McReynolds constants of the five probe compounds on an investigated column. As a result, the determined McReynolds constants (Table 1) of the TFT column suggested its weak polarity situated between the HP-5MS and DB-35 columns. Hence, these two commercial columns were employed as reference for the eval-