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Boron nitride nanotubes and their functionalization via quinuclidine-3-thiol with gold nanoparticles for the development and enhancement of the HPLC performance of HPLC monolithic columns

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ABSTRACT

In this paper, a new and effective method was described for attaching gold nanoparticles (Au-NPs) on to the surface of thiol-terminated Boron Nitride Nanotubes (BNNT) functionalized with quinuclidine-3-thiol, acting as a bridging agent. The quinuclidine-3-thiol was first grafted onto the surface of the BNNTs via strong interactions between the electron pair from the nitrogen atom of the quinuclidine structure and the electronic gap from the boron atom of the BNNT. The bare surface of Au-NPs facilitates to attach on the thiol group of the thiol-terminated BNNTs. These two nanomaterials (pristine BNNTs and Au-BNNTs) were then incorporated into a monolithic polymer. The obtained monolithic BNNT and AuBNNT stationary phases were very useful columns for the HPLC isocratic mode separation of a series of benzene and naphtalene derivatives. The retention on these two stationary phases was due to the different intermolecular interactions including the dispersion interaction (area of the delocalized π bond), the dipole–dipole interactions, and the electrostatic repulsion. The presence of Au-NPs on the BNNT surface improved significantly the retention and column efficiency for compounds with thiol groups in their structure. As well, it was shown that both retention and column efficiency linearly increased with the nanotube (NT) amount in the polymerization mixture. This manuscript thus established for the first time the fact that BNNT was a very useful nanomaterial for the development of novel HPLC stationary phases and increased the performance of classical equivalent C18 monolithic columns.

1. Introduction

The problem of particulate separation media is their inability to completely fill the space within the chromatographic column [1]. This contributes to peak broadening and decreased column efficiency. Introducing separation media with a higher degree of continuity consisting of a monolith or continuous bed, the void volume can be decreased to a minimum [1–3]. The most important feature of such media is that the mobile phase is forced to flow through the large pores of the medium. The silica-based monolith columns were first introduced by Nakanishi and Soga [4,5], Tanaka and co-workers [6] and Cabrera et al. [7]. Continuous beds made of polyacrylamide gel compressed in the shape of columns were introduced by Hjerten et al. [8,9]. In such monolithic structures the lack of small pores did not permit the separation of molecules with a small size due to the weak number of binding sites especially in an isocratic elution mode. Therefore it is necessary to develop novel monolithic structures to improve their efficiency for separation of small molecules in an isocratic mode. Due to unique properties of nanoparticles, such as their large surface-to-volume ratio and their properties that differ from those of corresponding bulk materials, the use of nanomaterials in separation science is growing rapidly [10–12]. Latex-functionalized monolithic stationary phases were developed for the separation of carbohydrates by micro-anion exchange chromatography [13] and for in-line sample preconcentration in capillary electrophoresis [14]. Silica nanoparticle – templated methacrylic acid monoliths were also used for in-line solid-phase extraction of basic analytes in capillary electrophoresis [15]. Incorporation of hydroxyapatite nanoparticles in monolithic columns was developed for separation of proteins and enrichment of phosphopeptides [16]. Gold nanoparticles were used as intermediate ligands for capillary columns with varying surface functionalities such as the pre-concentration of thiol containing peptides and the separation of proteins [17–19]. Carbon nanotubes (CNTs) [20–23] were used as stationary phase in GC [24–28], HPLC [29–33] and in electrochromatography [34] due to the non-covalent interaction established between the

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analyte and these nanostructured materials including electrostatic interactions (e.g. dipole–dipole), hydrogen bonds, π–π stacking, dispersion forces, dative bonds and the hydrophobic effect. CNTs were also incorporated in porous monolithic polymer to enhance the chromatographic separation of small molecules [35] and the performance of an arginase enzymatic reactor [36]. Tight-binding calculations have proposed that nanotubes might also be formed from hexagonal boron nitride (BN) [37]. Boron nitride nanotubes (BNNTs) were firstly synthesized in a plasma arc discharge apparatus similar to that used for carbon fullerene production [38]. Tubes of the sp^2 bonded hexagonal BN sheet material have thus now been successfully synthesized [39–41]. BN tubes provide therefore interesting possibilities for potential use in chromatography. Gold nanoparticles were attached at the surface of amine and thiol functionalized boron nitride nanotubes [42]. This paper demonstrated, for the first time, the use of BNNTs incorporated into a polymeric chromatographic support to enhance the performance of the HPLC isocratic mode separation quality for small size molecules. The molecular retention mechanism on this novel stationary phase was compared with the one obtained with BNNTs where Au-NPs were anchored on their surface functionalized with quinuclidine-3-thiol.

2. Experimental

2.1. Equipment

The HPLC system consisted of a Waters HPLC pump 501 (Saint-Quentin, Yvelines, France), an Interchim rheodyne injection valve, Model 7125 (Interchim, Montluçon, France), fitted with a reverse 20 (L sample loop, a Merck L4000 variable-wavelength UV spectrophotometer detector, and a Merck D2500 chromato – integrator (Nogent sur Marne, France). The chromatographic column tube (100 mm × 4.6 mm) was obtained from Interchim (Montluçon, France). Specific surface area and porosimetry of the chromatographic supports were determined by the Micromeritics' ASAP 2020 Accelerated Surface Area and Porosimetry Analyser (Micromeritics France SA, Verneuil en Halatte).

2.2. Reagents

Glycidyl methacrylate (GMA), ethylene dimethacrylate (EDMA), azobisisobutyronitrile (AIBN), 1-dodecanol, cyclohexanol, ethanol, HPLC grade solvents acetonitrile (ACN) were obtained from Sigma Aldrich (Paris, France). Trisodium citrate dehydrate ($C_6H_5O_7Na_3$), $HAuCl_4$, benzene (Ben), parabens (methyl paraben (MeP), ethyl paraben (EtP), propyl paraben (PrP), butyl paraben (BuP)) and naphthalene derivatives (naphtalene (N), naphthalene-1-thiol (N1T), naphthalene-2-thiol (N2T), dithionaphtalene (DTN), dimethyl(amino)naphthalene-1,8Bis (DMeAN)) where obtained from Sigma Aldrich (Paris, France). Quinuclidine-3-thiol (1-Azabicyclo [2] octane-3-thiol) was obtained from Axyntis (Paris, France). All chemicals were used as received with the exception of EDMA and GMA which were redistilled before use to remove inhibitors. Water was obtained from an Elgastat water purification system (Odil, Talant, France), fitted with a reverse osmosis cartridge. BNNTs was obtained from the Australian National University (Canberra, Australia) (yield >80%, boron nitride >97 wt%; typical diameter 50 nm and length >1 μm).

3. Method

3.1. Preparation of gold nanoparticles

A 100 mL of 1 mM aqueous $HAuCl_4$ was reduced by 20 mL of 1 mM $C_6H_5O_7Na_3$ at 100 °C, when the color changes from pale yellow to fresh red, the solution was removed from the hot plate at that moment and cooled down at room temperature. A colloidal solution containing AuNPs of ∼10 nm diameter to sidewalls was thus obtained.

3.2. Preparation of thiol functionalized BNNT

Thiol-functionalized BNNTs (BNNT-SH) were prepared by the following reaction by the use of quinuclidine-3-thiol which could be bound on to surface of BNNT through the strong interaction between the electron pair from the nitrogen atom of the quinuclidine structure and the electronic gap from the boron atom of the BNNT. The raw BNNT (200 mg) suspended in 10 mL of quinuclidine-3-thiol was stirred magnetically and refluxed in the dark place for 24 h at 120 °C. The mixture was subsequently filtered and the as-obtained filtered solid was further dried under dynamic vacuum oven for 24 h at 70 °C.

3.3. Attachment of gold nanoparticles onto BNNTs

The BNNT-SH (20 mg) was added to the 20 mL ethanol under vigorous stirring condition and then the 20 mL of 1 mM colloidal Au solution was subsequently added to the BNNTs/ethanol solution. After one day, the product (Au–BNNT–SH complex) was filtered and washed several times with distilled water and finally dried in vacuum over a night.

3.4. Incorporation of BNNTs or AuBNNTs into the monolithic chromatographic support

The monolithic stationary phase was directly prepared by in situ polymerization within the chromatographic column tube. The method was similar as the one described by Andre et al. [36] or Chambers et al. [35] for the incorporation of carbon nanotubes in poly(glycidyl methacrylate-ethylene dimethacrylate) monoliths. Glycidyl methacrylate (28% (m/m)), ethylene dimethacrylate (12% (m/m)) and a small specific amount of BNNT (or AuBNNT) × (% (m/m)), were added in the appropriate porogenic agents 1-dodecanol (6% (m/m)) and cyclohexanol (53.2% (m/m)). After mixing a homogeneous solution was obtained due to the dispersion of BNNT or Au-BNNT-SH. Then, azobisisobutyronitrile (0.8% (m/m)) was added to the mixture. The solution was then sonicated for 30 min, purged with nitrogen gas for 15 min at 25 °C to remove oxygen. The ends of the stainless-steel tube were connected with plastic tubes and then sealed at the bottom, filled with the above polymerization mixture and then sealed at the top. Subsequently, the polymerization was performed in a water bath at 51 °C for 24 h. After the polymerization, the seals and plastic tubes were removed. The two columns (BNNTC and AuBNNTC) obtained were provided with fittings, and connected to an HPLC pump. As well, a blank column (BC) with no BNNTs or AuBNNTS incorporated in the polymerization mixture was synthesized.

4. Results and discussion

4.1. BNNT, BNNT-SH and AuBNNT spectral characterization

The BNNT, BNNT-SH and the AuBNNT samples were characterized by Raman and Fourier infrared (FTIR) spectroscopy. For the BNNT FTIR spectra, three absorption frequency regimes can be distinguished at 808, 1370 and 1535 cm^{-1}. All these optical spectra are the fingerprints of BNNTs [43]. For the BNNT-SH spectra additional peaks were observed. A peak at 2556 cm^{-1} confirmed the presence of a thiol group at the end and on the sidewalls of the BNNTs. The peaks observed around 1458 cm^{-1} and 2000 cm^{-1} are the two principal absorption peaks of quinuclidine [44]. For

the AuBNNT spectra, the characteristic stretching modes of thiol groups with broad range had vanished. It indicates that the gold nanoparticles are assembled to nanotubes via noncovalent interaction between —SH groups of thiol-terminated BNNTs and Au-NPs to form AuBNNT complex.

The monolithic support with no BNNTs prepared at 51 °C exhibit a surface area of 43 m^2/g. The pore size was 2.04 μm. Addition of a small amount of BNNT or AuBNNT to the polymerization mixture affords no significative change in surface areas and pore size for 0.05% and 0.40% of BNNT or AuBNNT. This finding is corroborated with negligible change in the back pressure of the column that remains ±3% at all tested flow rate.

4.2. BNNTC and AuBNNTC stability

The BNNT and AuBNNT column (i.e., BNNTC and AuBNNTC) stability was tested for 0.4% of NT into the polymerization mixture by comparing the column efficiency and the retention factor determined with naphthalene-2-thiol during the study and after four months in the same conditions, i.e., a mixture of ACN and water (55/45) %(v/v) as mobile phase, a flow rate of 0.4 mL/min, a temperature equal to 25 °C and a back pressure of 7 bar. The height equivalent to a theoretical plate and the retention factor of naphthalene-2-thiol were respectively equal to 6.8 μm and 4.00 with BNNTC and 5.52 μm and 6.72 with AuBNNTC. The maximum relative difference between these values was never more than 0.5% proving the stability of the BNNTC and AuBNNTC during an extended period of time.

4.3. Benzene and naphthalene derivatives-BNNT (or -AuBNNT) association mechanism

With the BNNTC the retention factor obtained was in the sequence: Ben < MeP < EtP < PrP < BuP < N< N2T ≅ N1T < DTN < DMeAN (see Fig. 1). It appeared that BNNTC had lower affinity for benzene derivatives than for naphthalene derivatives. These results demonstrated that a planar conformation was important for the retention on the BNNT stationary phase and the sp^2 bonded hexagonal BN sheet material developed with polycyclic aromatic derivatives polar interactions ((–(stacking). Zhao et al. [45] demonstrated that the center of aromatic rings tend to locate on top of the nitrogen site of BNNT. They demonstrated that the trend of adsorption energy for the aromatic rings on the BNNTs showed marked dependence on different intermolecular interactions, including the dispersion interaction (area of the delocalized π bond), the dipole–dipole interaction (polarization), and the electrostatic repulsion (lone pair electrons). To gain further insight into this molecule-BNNT (and -AuBNNT) association mechanism the previous experiments were carried out at four other temperatures (i.e., 5 °C, 10 °C, 30 °C, 40 °C). The molecule-BNNT (and AuBNNT) association mechanism enthalpy was calculated using the slopes of the plot lnk vs (1/*T*) (van'T Hoff plots). Table 1 presents the ΔH° values for all molecules. The interaction enthalpies for all the solute molecules with BNNT and AuBNNT were exothermic and consequently favorable for their association with BNNT and AuBNNT. As well, it was observed that the enthalpy value determined on the AuBNNT phase was the lowest for compounds with thiol groups. This confirmed that the Au-NPs immobilized on BNNTs exhibited with thiol groups favorable non specific interactions and increased the retention of compounds containing —SH in their molecular structure. This result was also supported by the retention order of the solute molecules on the AuBNNT stationary phase, i.e., Ben < MeP < EtP < PrP < BuP < N < DMeAN < N1T < N2T < DTN (see Fig. 1). The retention order of the alkyl parabens (i.e., an increase in retention was observed with the number of carbon atom on the alkyl chain) on BNNT and AuBNNT can be explained by the fact that hydrophobic effects additive to the polar interactions were implied in the molecule association mechanism on BNNT and AuBNNT. This result was confirmed by the fact that increasing the ACN percentage in the mobile phase reduces the retention factor of the solute molecules on the BNNT and Au-BNNT stationary phases (Fig. 2).

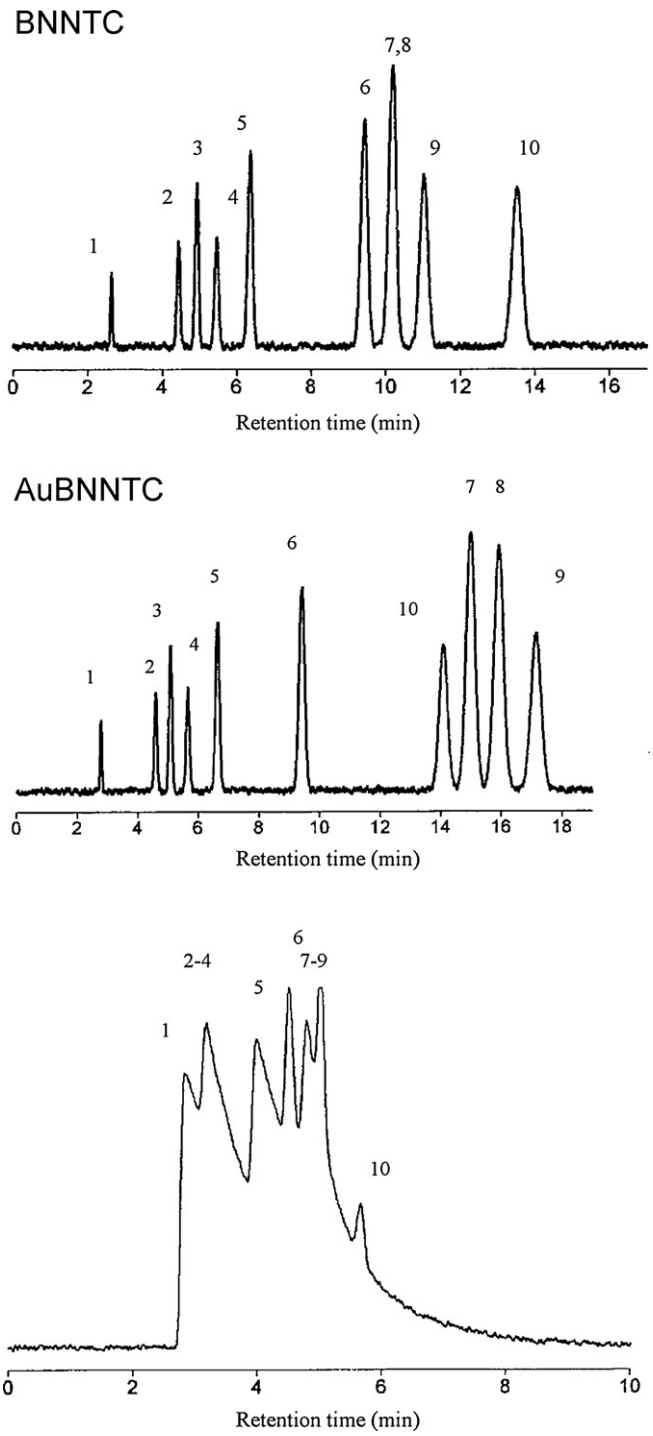

Fig. 1. HPLC chromatograms for the separation of (1) Ben (2) MeP (3) EtP (4) PrP (5) BuP (6) N (7) N1T (8) N2T (9) DTN (10) DMeAN on the BNNTC, AuBNNTC and the Chromatographic conditions: Column: 100 mm × 4.6 mm i.d./0.4% NT; Mobile phase: ACN/H_2O (55/45) (v/v); Flow rate: 1 mL/min; Column temperature: 25 °C; Detection wavelength: 254 nm; (number refers to peak on the chromatograms).

Table 1
ΔH (kJ mol^{-1}) values for the binding mechanism of benzene and naphthalene derivatives with the BBNT and Au BNNT stationary phases.

Solute molecule	ΔH (kJ mol^{-1})$_{BNNTC}$	ΔH (kJ mol^{-1})$_{AuBNNTC}$
Ben	−14.1	−14.7
MeP	−21.2	−22.8
EtP	−26.8	−28.9
PrP	−29.6	−30.0
BuP	−33.1	−33.5
N	−50.5	−48.0
N1T	−53.4	−70.7
N2T	−53.7	−74.4
DTN	−60.9	−79.8
DMeAN	−68.0	−69.9

4.4. BNNTC and AuBNNTC efficiency

The separation of the solute molecules on the three columns, i.e., the BC, BNNTC, and AuBNNTC was now analyzed. No separation was observed on the BC (Fig. 1). At a content of 0.4% NT, an excellent separation was observed on the AuBNNTC but no separation was observed between naphthalene-2-thiol and naphthalene-1-thiol on the BNNTC (Fig. 1). Sharp and symmetrical peaks were obtained for all peaks on the chromatograms (Fig. 1). The asymmetry factor reflecting the peak distortion determined by calculating the first part of the peak at 10% of the peak height was equal to 1.00 for all peaks. Fig. 3 showed the Knox curves for BNNTC and AuBNNTC for a 0.4% content of NT and the Knox curve for a conventional chromolith C18 column (Performance RP-18, 100 mm × 4.6 mm, 2 μm macropore size, Merck KGaA, Darmstadt, Germany). The comparison showed that the lowest efficiency was observed for the C18 chromolith column. The Knox plot of the BNNTC and AuBNNTC demonstrates clearly that the separation efficiency does not increase significantly when the flow rate is increased as is the case with traditional particulate columns. It is thus possible to operate at high flow rates with minimal loss of peak resolution. Incorporation of NT into the polymeric mixture (the BBNTC and AuBNNTC) results in an increase in both retention and efficiency. To confirm these results, 14 other columns (7 BNNTCs and 7 AuBNNTCs) were developed where the amount of NT (x%) (BNNT or AuBNNT) into the polymerization mixture was equal to 0.05; 0.1; 0.15; 0.20; 0.25; 0.3; 0.35. Beyond 0.40%, NT dispersed with great difficulties in the polymerization mixture and the obtained polymer tends to crack. Figs. 4 and 5 represented respectively the variation of the retention factor (k), the height equivalent to a theoretical plate (h) for naphthalene-2-thiol versus x on the two columns. Figs. 4 and 5 confirmed that increasing the amount of NT in the polymerization mixture enhanced both the retention and h. These results are similar to those observed by Chambers et al. [35] for a monolithic column containing entrapped carbon nanotubes. However no study was made concerning the entrapment of boron nitride nanotubes.

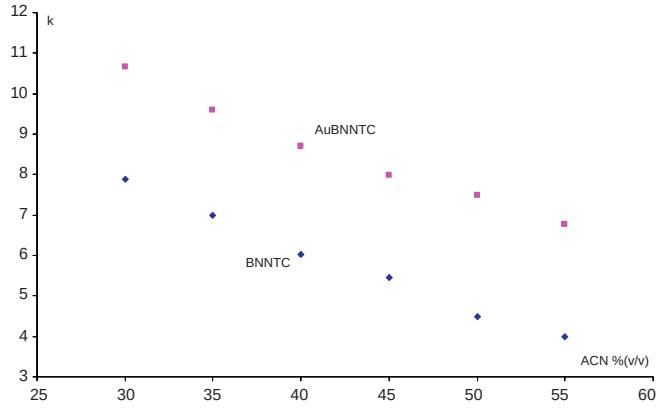

Fig. 2. k for naphthalene-2-thiol vs the percentage of ACN in the ACN/H_2O (v/v) mixture on the BNNTC and AuBNNTC (see experimental conditions in Fig. 1).

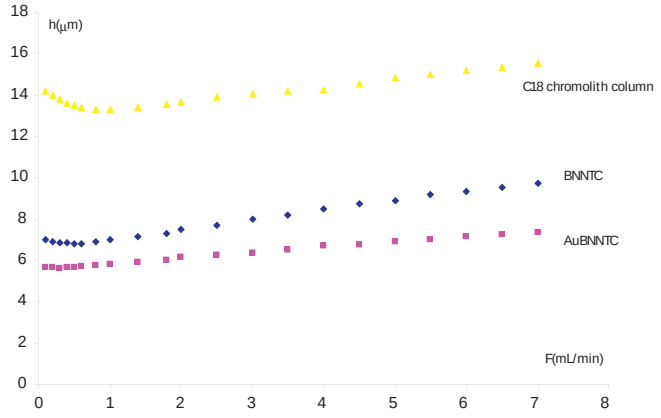

Fig. 3. A van Deemter plot of the height equivalent to a theoretical plate h (μm) vs flow-rate F (mL/min) for BNNTC, AuBNNTC (for a 0.4% of NT) and an equivalent classical C18 chromolith performance column.

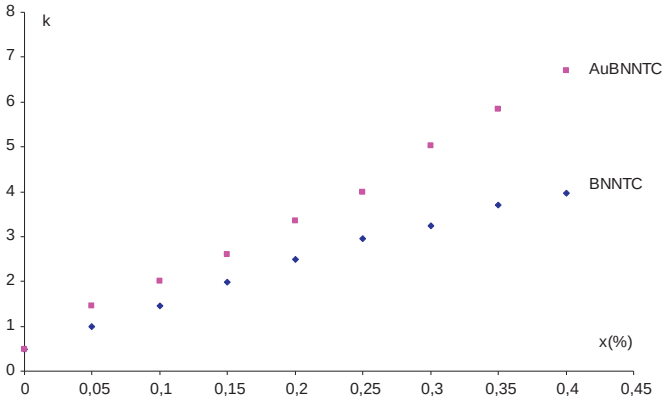

Fig. 4. k for naphthalene-2-thiol vs the percentage of BNNT or AuBNNT incorporated into the polymerization mixture x (%) for BNNTC and AuBNNTC. See experimental conditions in Fig. 1.

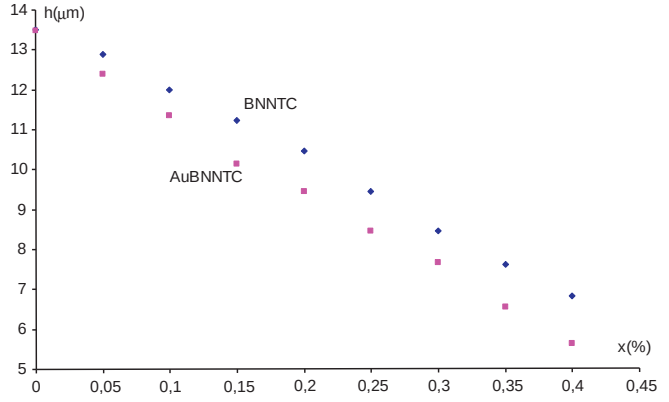

Fig. 5. Height equivalent to a theoretical plate, h (μm), for naphthalene-2-thiol vs the percentage of BNNT or AuBNNT incorporated into the polymerization mixture x (%) for BNNTC and AuBNNTC.

5. Conclusion

This work demonstrated that the incorporation of a small amount of BNNT into a monolithic chromatographic support increases both retention and column efficiency and allows the

separation of a series of small molecules in an isocratic HPLC elution mode. The molecular recognition mechanism on this novel stationary phase was due to specific interactions including the dispersion interaction, the dipole–dipole interactions and the electrostatic repulsion. As well, a new and efficient method was described to attach gold nanoparticles (Au-NPs) on to the surface of boron nitride nanotubes functionalized with quinuclidine-3-thiol. The mixture of benzene and naphthalene derivatives was especially fully separated on the AuBNNTC with sharp and symmetrical peaks due to non specific covalent interactions between Au-NPs immobilized on the BNNT surface and thiol groups of some compounds to be separated. The present work thus showed clearly the advantages of these novel monolithic columns based on BNNT and Au-NPs nanomaterials in comparison with classical C18 monolithic columns for the HPLC isocratic separation of small molecules.

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Glossary

AIBN: azoisobutyronitrile
AuBNNTC: gold nanoparticle boron nitride nanotube column
Au-BNNT: boron nitride nanotube functionalized with gold nanoparticles
Au-NP: gold nanoparticle
BC: blank column
Ben: benzene
BNNT: boron nitride nanotube
BNNTC: boron nitride nanotube column
BNNT-SH: boron nitride nanotube functionalized with thiol groups.
BuP: butyl paraben
DMeAN: dimethyl(amino)naphthalene-1,8Bis
DTN: dithionaphtalene
EDMA: ethylene dimethacrylate
EtP: ethyl paraben
GMA: glycidyl methacrylate
MeP: methyl paraben
N: naphtalene
NP: nanoparticle
NT: nanotube
N1T: naphthalene-1-thiol
N2T: naphthalene-2-thiol
PrP: propyl paraben