



Synthesis of a dendrimeric phenoxy-substituted cyclotetraphosphazene and its non-covalent interactions with multiwalled carbon nanotubes



Elif Okutan^{a,b}, Bünyemin Çoşut^a, Saadet Beyaz Kayıran^c, Mahmut Durmuş^a, Adem Kılıç^a, Serkan Yeşilot^{a,*}

^a Department of Chemistry, Gebze Institute of Technology, 41400 Gebze, Kocaeli, Turkey

^b Department of Chemistry and Pharmacy, Friedrich-Alexander Universität Erlangen, Nürnberg, 91054 Erlangen, Germany

^c Department of Chemistry, Kocaeli University, 41380 Kocaeli, Turkey

ARTICLE INFO

Article history:

Received 13 May 2013

Accepted 2 September 2013

Available online 21 September 2013

Keywords:

π - π stacking

Phosphazene

Carbon nanotube

ABSTRACT

A dendrimeric phenoxy-substituted cyclotetraphosphazene has been prepared for the non-covalent functionalization of multiwalled carbon nanotubes (MWCNTs). The synthesized cyclotetraphosphazene derivatives (**2–4**) and dendrimeric cyclotetraphosphazene (**5**) have been characterized by standard spectroscopic techniques. The functionalization of MWCNTs with compound **5** has been accomplished and the resulting MWCNT-5 hybrid has been characterized by ³¹P NMR, ¹H NMR, Raman spectroscopy, X-ray diffraction (XRD), energy dispersive X-ray (EDX), fluorescence, thermal gravimetric analysis (TGA) and high-resolution transmission electron microscopy (HRTEM) techniques. The results showed that the dendrimeric compound **5** has been attached to the MWCNTs via non-covalent " π - π " interactions between the phenoxy groups on the dendrimeric compound **5** and the extended π system of the MWCNTs. The MWCNT-5 hybrid exhibited significant dispersion stability in common organic solvents.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs) have attracted particular interest since their discovery in the 1990s because of their extraordinary properties [1]. CNTs have been incorporated into many application areas, such as optoelectronics, nanotechnology and chemical sensing [2–4]. The key problem for the application of CNTs is their poor solubility, which is caused by bundling of carbon nanotube walls owing to van der Waals interactions between the walls of CNTs [5]. To this end, many surface modification approaches have been proposed to address the solubility problem of CNTs, including covalent and non-covalent functionalization [6–10]. Whilst non-covalent functionalization can be achieved without destroying the extended π -network of CNTs, covalent functionalization results in permanent structural modification of CNTs, which may cause a loss of their unique properties [11]. Among the many non-covalent solubilization approaches, the sorption of aromatic compounds on CNTs has been studied by several groups [12,13]. Aromatic compounds can interact strongly with the graphitic walls of CNTs through effective π - π stacking [14]. The size, shape and the environment of the aromatic system generally affects the affinity of

the π - π interaction [15]. So far, polynuclear aromatic compounds [16,17], conjugated polymers [18] and also dendrimers like phthalocyanine [19] and porphyrin [20] have been used to modify CNTs. Dendrimers have drawn considerable attention for the functionalization of CNTs because of their size, symmetric, highly branched and non-entangled architecture [21]. For instance, dendrimeric cyclophosphazene frameworks can provide valuable advantageous purposes towards useful materials for CNT-dendrimeric phosphazene materials.

The multi-functional nature of chlorocyclophosphazenes allows these compounds to be utilized as dendrimer cores [22]. N₃P₃Cl₆ and N₄P₄Cl₈ offer six and eight branching points respectively, which is significantly more than the ones available with conventional organic cores. Additionally, depending on the nature of the side groups, cyclic phosphazene derivatives and macromolecules show high chemical and thermal stabilities and they can also display various properties suitable for a wide range of applications [23–28]. Even though some poly(organophosphazenes) have been successfully used for the coating of CNTs based on non-covalent interactions [8,29–31], dendrimeric cyclic phosphazene-CNT hybrid materials have not been reported. In our previous works, we have demonstrated that poly(organophosphazene)s are very attractive candidates for an advanced dispersing agent of carbon nanotubes [8,9]. Poly(organophosphazenes) are reasonably flexible and usually possess a linear or branched structure, which may lead to relatively unstable dispersions because they can wrap

* Corresponding author. Address: Department of Chemistry, Gebze Institute of Technology, P.O. Box: 141, Gebze 41400, Kocaeli, Turkey. Tel.: +90 262 6053137; fax: +90 262 6053101.

E-mail address: yesil@gyte.edu.tr (S. Yeşilot).

themselves around either nanotubes or nanotube bundles. CNT-dendrimeric cyclophosphazene systems which disrupt the van der Waals interactions that cause the insolubility of CNTs show promise. In this respect, the development of new non-covalent CNT-dendrimeric cyclophosphazene hybrid materials showing high thermal stability and solubility in widely used solvents would be important for the applications of CNT-based systems.

In this research, procedures of non-covalently introducing a phenoxy-substituted dendrimeric cyclophosphazene (**5**) onto the side walls of MWCNTs by non-covalent adsorption and the spectroscopic, thermal and morphological properties of the soluble MWCNT-5 nanocomposite, using ^{31}P NMR, XRD, EDX, TGA and HRTEM techniques, are reported. The fluorescence, Raman and ^1H NMR spectra confirmed the non-covalent functionalization of MWCNTs with phenoxy groups on the dendrimeric compound. The hybrid material shows both high thermal stability and excellent fluorescence quenching efficiency. Also the hybrid (MWCNT-5) showed significant dispersion stability in common organic solvents, such as dichloromethane, chloroform, *N,N*-dimethylformamide, dimethyl sulfoxide and tetrahydrofuran.

2. Experimental

2.1. Materials

Octachlorocyclophosphazene (Otsuka Chemical Co. Ltd.) was purified by fractional crystallization from *n*-hexane. The deuterated solvents (CDCl_3 and toluene- d_8) for NMR spectroscopy and the following chemicals were obtained from Merck; cyclohexene, ethanol, phenol, $\text{Pd}(\text{OH})_2$, Cs_2CO_3 , NaH, acetone, triethylamine, silica gel 60, tetrahydrofuran $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, MgO and HCl (37%). 1,8,9-Anthracenetriol for the MALDI matrix was obtained from Fluka. Acetylene (99.8%), helium (99.98%) and hydrogen (99.998%) gases were purchased from Yalız Industrial Medical Gases Inc.

2.2. Equipment

Elemental analyses were carried out using a Thermo Finnigan Flash 1112 Instrument. UV-Vis spectra were recorded with a Shimadzu 2101 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Mass spectra were acquired in linear modes with an average of 50 shots on a Bruker Daltonics Microflex mass spectrometer (Bremen, Germany) equipped with a nitrogen UV-Laser operating at 337 nm. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g. crude mixture, 100 g. silica gel was used in a column 3 cm in diameter and 60 cm in length) and preparative thin layer chromatography was performed on silica gel 60 P F_{254} . ^1H , ^{13}C and ^{31}P NMR spectra were recorded in CDCl_3 and toluene- d_8 solutions on a Varian 500 MHz spectrometer. The thermal properties of the compounds were investigated on a Mettler Toledo TGA/SDTA 851 Thermogravimetric Analysis (TGA) instrument. The X-ray diffraction (XRD) patterns of the samples were taken at room temperature with $2\theta = 5\text{--}40^\circ$ on a BRUKER D8 Advance X-ray diffractometer equipped with a sealed tube copper target (λ Cu $K\alpha = 1.54056 \text{ \AA}$). The structural analysis was performed on an automated Renishaw InVia Reflex Raman microscopy system (Renishaw Plc., New Mills, Wotton-under-Edge, UK) equipped with a 514 nm laser, which was used for all of the experiments. The morphology of the composite (MWCNT-5) was characterized using a Philips-FEI G2 F20 S-Twin HRTEM. The NMR simulation program, available free of charge, used was gNMR [32].

2.3. Synthesis

1,1,3,3,5,5,7,7-Octaphenoxy-cyclophosphazetetraene, $[\text{NP}(\text{OC}_6\text{H}_5)_2]_4$, (**1**) was prepared according to procedures described previously [33].

2.3.1. Synthesis of compound (**2**)

A solution of sodium phenoxide was prepared by the dropwise addition of phenol (2.1 g, 23 mmol) to a sodium hydride (1.1 g, 28 mmol, 60%) dispersion in dry THF (60 mL) at 0°C . Octachlorocyclophosphazene (1.6 g, 3.3 mmol) in dry THF (30 mL) was added dropwise to the reaction mixture of sodium phenoxide, and the resulting mixture was stirred for 0.5 h. The reaction mixture was then stirred for 1 day under an atmosphere of argon and the reaction was followed by TLC. Sodium chloride was removed by filtration, the solvent was removed under reduced pressure and the resulting product was subjected to column chromatography using benzene:petroleum ether (1:1) as the eluent. Yield: 2.5 g (80%). *Anal. Calc.* for $[\text{C}_{42}\text{H}_{35}\text{Cl}_8\text{N}_4\text{O}_7\text{P}_4]$ Found: C, 58.26; H, 4.10; N, 6.40%; requires: C, 58.18; H, 4.07; N, 6.46%. MS (ESI) *m/z* (%) *Calc.*: 866; found: 867 (100) $[\text{M}+\text{H}]^+$. $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8), assigned as an AB_2C spin system δ : -4.064 [1P, P(OPh)Cl, A], -11.65 [2P, P(OPh) $_2$, B $_2$], -11.05 [1P, P(Ph) $_2$, C], $^2J_{\text{AB}} = 55 \text{ Hz}$, $^2J_{\text{AC}} = 18 \text{ Hz}$, $^2J_{\text{CB}} = 79 \text{ Hz}$. ^1H NMR (CDCl_3) δ : 7.01–7.29 (m, 35H, ArCH). $\{^1\text{H}\}^{13}\text{C}$ NMR (CDCl_3) δ : 151.40 (ArC), 144.30 (ArC), 129.53 (ArCH), 125.44 (ArCH), 124.90 (ArCH), 121.77 (ArCH), 121.28 (ArCH).

2.3.2. Synthesis of compound (**3**)

4-(Benzyloxy) phenol (0.54 g, 2.7 mmol), dry and finely powdered cesium carbonate (0.91 g, 2.8 mmol) were dissolved in dry THF (10 mL) under an argon atmosphere. The solution was transferred into a dropping funnel (50 mL) and slowly dropped into a solution of 1,1,3,3,5,5,7-heptaphenoxy-7-chlorocyclophosphazetetraene (2 g, 2.3 mmol) (**2**) in dry THF (10 mL) under an argon atmosphere in a three necked round bottomed flask (50 mL). The reaction mixture was refluxed under argon for 24 h and followed by TLC, until it indicated that no starting material remained. The precipitated salt (CsCl) was filtered off and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using silica gel 60 (70–230 mesh) as the adsorbent and dichloromethane:*n*-hexane (1:2) as the eluent. 1,1,3,3,5,5,7-Heptaphenoxy-7-[(4-benzyloxy)phenoxy]-cyclophosphazetetraene (**3**) was obtained as a viscous oil; Yield: 1.65 g (68%). *Anal. Calc.* for $[\text{C}_{55}\text{H}_{46}\text{N}_4\text{O}_9\text{P}_4]$ Found: C, 64.16; H, 4.55; N, 5.36%; requires: C, 64.08; H, 4.50; N, 5.43%. MS (ESI) *m/z* (%) *Calc.*: 1030; found: 1163 (100) $[\text{M}+\text{Cs}]^+$. $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8) δ : -12.45 (br, s, 4P). ^1H NMR (CDCl_3) δ : 6.61–7.33 (m, 44H, ArCH), 4.89 (br s, 2H, CH_2). $\{^1\text{H}\}^{13}\text{C}$ NMR (CDCl_3) δ : 155.69 (ArC), 151.60 (ArCH), 145.37 (ArC), 137.28 (ArC), 129.39 (ArCH), 128.87 (ArCH), 127.68 (ArCH), 124.56 (ArCH), 121.26 (ArCH), 115.38 (ArCH), 70.64 (CH_2).

2.3.3. Synthesis of compound (**4**)

1,1,3,3,5,5,7-Heptaphenoxy-7-[(4-benzyloxy)phenoxy]-cyclophosphazetetraene (**3**) (1.05 g, 1 mmol) was dissolved in dry THF (10 mL) under an argon atmosphere and cyclohexene (10 mL), palladium (II) hydroxide (0.4 g, 20 wt% on carbon) and ethanol (10 mL) were added to this solution. The mixture was refluxed for 24 h under an argon atmosphere and filtered. All of the solvents were removed under reduced pressure. 1,1,3,3,5,5,7-Heptaphenoxy-7-[(4-hydroxy)phenoxy]cyclophosphazetetraene (**4**) was obtained by crystallization from dichloromethane/*n*-hexane (1:1); Yield: 0.75 g (78%). *Anal. Calc.* for $[\text{C}_{48}\text{H}_{40}\text{N}_4\text{O}_9\text{P}_4]$ Found: C, 61.33; H, 4.35; N, 5.89%; requires: C, 61.28; H, 4.29; N, 5.96%. MS (ESI) *m/z* (%) *Calc.*: 940; found: 963 (100) $[\text{M}+\text{Na}]^+$. $^{31}\text{P}\{^1\text{H}\}$ NMR

Download English Version:

<https://daneshyari.com/en/article/1335488>

Download Persian Version:

<https://daneshyari.com/article/1335488>

[Daneshyari.com](https://daneshyari.com)