Structural, chemical and electrical characterization of organocyclotriphosphazene derivatives and their graphene-based composites

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**Abstract**

In the present work, new di-spiro and tetra-spiro organophosphazene compounds (DPP-Ant-1 and 2, BPP-Ant-1 and 2) were synthesized by interaction with conjugate anthracene-substituted chalcone compounds (Ant-1 and 2) with organocyclotriphosphazene compounds DPP and BPP. All the compounds were fully characterized and confirmed by elemental analysis, spectroscopic and thermal techniques such as DSC, TGA, mass, FT-IR, 1H, 13C-APT, 31P NMR and 2D HETCOR NMR. These organocyclotriphosphazenes were designed and synthesized in order to investigate the changes in the conductive properties of graphene-based compounds. The graphene-based materials have a wide range of technological applications such as electronics, optics, thermal and mechanical properties. Graphene-based phosphazenes composites were prepared. The AC and DC conductivity of graphene-based phosphazene composites were measured. Dielectric measurements (dielectric constant, dielectric loss factors and conductivity) of organophosphazene compounds were measured against increasing frequency (range from 100 Hz to 20 kHz at 25 °C) at different temperature (between 298 and 348 K) using means of an impedance analyzer and then and compared with each other. Also, the activation energy profile of graphene/phosphazene composites was revealed by measuring DC conductivity of an individual composite material. The obtained graphene/phosphazene composites have been found that they have a semiconductor property according to the DC conductivity results.

1. Introduction

One of the most interesting groups of chemical compounds that contain a phosphorus-nitrogen bond is the series known as phospho-nitrilic compounds or, more commonly, phosphazenes. Phosphazenes are a homologous series of compounds which contain consecutive phosphorus and nitrogen atoms, with alternating single and double bonds between the two elements [1–3]. Because of its facile availability and physical properties, hexachlorocyclotriphosphazene is used as the starting material for the synthesis of organo-phosphazenes. The chlorophosphazene can undergo macromolecular substitution wherein all of its chlorine atoms are replaced by a suitable nucleophile via either a bimolecular or unimolecular mechanism. It is possible to give substitution reactions due to the reactivity of the –Cl atoms present in the structure of hexachlorocyclotriphosphazene (N3P3Cl6) and substitution reactions generally take place with nucleophilic oxygen, nitrogen and the sulfur atom in alkoxides, amines, thiols and aryl oxides [3–10]. When previously mentioned organic groups are bonded to each phosphorus atom, the phosphazene skeleton is stabilized against hydrolytic attack.

The organophosphazenes have generated considerable research interest in recent years because of their unusual physical and chemical properties. The properties of phosphazenes to be easily tailored by simply changing the side groups according to the desired structure-property relationship. Due to various properties of phosphazenes, they are potential to be applied in a wide range of applications [1–3]. Altering chlorine atoms with various organic groups make phosphazenes possessing diverse properties including high refractive index [11], dielectric properties and proton conductivity [12–14], cathode material for rechargeable lithium batteries [15], dye-sensitized solar cells [16], photodiodes [17], flame retardancy [18], biocompatibility, hydrophobicity, hydrophilicity, bioactivity, etc [19–23].
The studies related to the synthesis and electrical behavior of organocyclophosphazene derivatives were reported in the literature [24–31]. But no studies were found about new chalcone-substituted organocyclophosphazenes containing anthracene groups and their graphene-based composites.

For this reason, in this study, we aimed to synthesize highly conjugated anthracene containing chalcone-substituted organocyclophosphazenes (BPP-Ant-1 and 2, DPP-Ant-1 and 2). The conjugation and dipolar functional groups in the structures have a significant effect on the dielectric constant. The phosphazene/graphene nanocomposites were obtained by doped with nano-graphene of these synthesized compounds at 32 (w/w) ratios using a hydrothermal system. The electrical properties of both pure compounds (BPP-Ant-1 and 2, DPP-Ant-1 and 2) and their graphene-based compounds (phosphazene/graphene nanocomposites) were investigated. The dielectric measurements were taken up to the melting point by means of impedance analyzer at 100 Hz and 20 kHz depending on the alternating current (AC) conductivities and compared to one another. Furthermore, in the present study, AC and DC electrical properties and estimate the activation energy profile by measuring the DC conductivity of different graphene/phosphazene composites were reported. As a result, they have been found that graphene-doped phosphazene composites gained semiconductivity. These properties make graphene/phosphazene composites possible material for optoelectronic and other related applications.

2. Experimental

2.1. Materials and methods

9-Antaldehyde, 4'-hydroxyacetophenone and 9-acetylanthracene was purchased from Jkchemicals, Alfa Aesar, and Acros, respectively. 4'-Hydroxybenzaldehyde, hexachlorocyclophosphazene (HCCP) and sodium hydroxide (NaOH) were supplied from Sigma-Aldrich. Potassium carbonate (K₂CO₃) and K₂HPO₄ were obtained from Merck. Graphene nanoplatelet (3 nm, S.A: 530 m²/g, Dia: 1.5 μm) was purchased from Nanography Nanotechnology research institute (Ankara/Turkey).

FT-IR spectra of all compounds were recorded with a Perkin Elmer FT-IR instrument using KBr pellets. ¹H, and ¹³C NMR spectra of the compounds were analyzed using a Bruker DPX-400 spectrometer. Elemental analysis was carried out by a LECO 932 carbon and hydrogen analyzer.

2.2. Synthesis

2.2.1. Synthesis of 1-(anthracen-9-yl)-3-(4-hydroxyphenyl)prop-2-en-1-one compound (Ant-1)

9-Acetylanthracene (13.62 mmol) was dissolved in ethanol (80 mL) and 50% NaOH solution (15 mL) was added to the mixture and stirred at 30 min. 4'-Hydroxybenzaldehyde (13.82 mmol) was added to the reaction mixture at room temperature. The completion of reaction was monitored by TLC and was taken 12 h. Part of ethanol was evaporated and residue precipitated in water and acidified with 2 N HCl to pH 4–5 range for full precipitation. The mixture was filtered and washed with warm water several times. The yellow solid was obtained. Yield 3.52 g (80%). M.p.: 263–264 °C. Anal. Calc. for C₉H₈O₂: C, 85.16; H, 4.97.

2.2.2. Synthesis of 1-(anthracen-9-yl)-3-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-one compound (Ant-2)

The Synthesis of Ant-2 was prepared similar to the procedure used in the preparation of Ant-1 and was prepared using 9-Acetylanthracene (13.62 mmol), 4'-hydroxybenzaldehyde (13.82 mmol) and 50% NaOH solution (15 mL) for 16 h. Yield: 4.28 g (89%). M.p.: 151–152 °C. Anal. Calc. for C₂₀H₁₇O₃ (345.40): C, 81.34; H, 5.12. Found: C, 81.39; H, 5.16%. FT-IR (KBr, cm⁻¹): 3393, 3033, 3057 and 3077 versus (C=H, Aliphatic), 1644 versus (C=O), 1626, 1619, 1594, 1587, 1572 and 1510 versus (C=N). The Synthesis of Ant-2 was prepared similar to the procedure used in the preparation of Ant-1 and was prepared using 9-Acetylanthracene (13.62 mmol), 4'-hydroxybenzaldehyde (13.82 mmol) and 50% NaOH solution (15 mL) for 16 h. Yield: 4.28 g (89%). M.p.: 151–152 °C. Anal. Calc. for C₂₀H₁₇O₃ (345.40): C, 81.34; H, 5.12. Found: C, 81.39; H, 5.16%. FT-IR (KBr, cm⁻¹): 3393, 3033, 3057 and 3077 versus (C=H, Aliphatic), 1644 versus (C=O), 1626, 1619, 1594, 1587, 1572 and 1510 versus (C=N).
then HCCP (10.2 g, 29.38 mmol) in inert atmosphere. The reaction mixture was stirred at room temperature for 15 min. Acetone was evaporated in rotary evaporator, and the residue was extracted with chloroform (3 × 50 mL). Evaporation of chloroform in rotary evaporator gave BPP as a white solid, yield 90% (12.17 g). Recrystallization from dichloromethane/petroleum ether (2/1) gave the pure product. M.p.: 194–195 °C. Anal. Calc. for C_{38}H_{43}NO_3P_2: C, 77.48; H, 4.25; N, 2.61. Found: C, 77.49; H, 4.30; N, 2.66. MALDI-MS: m/z calc. 1612.62, found: 1613.45 [M+H]^+ . FT IR (KBr, cm⁻¹): 3008, 3035 and 3048 ν(ν_C-H) 2937 and 2956 ν(ν_C-H). 1643 ν(C-O), 1502, 1577, 1556 and 1624 ν(C= C), 1162, 1179 and 1200 ν(ν_P-O). 948 ν(ν_C-O). 31P NMR (DMSO-d_6): 9.28 (2P, d, P(O-C_2_2H_4)), 24.24 (1P, t, P(O-C_2_2H_4)). H NMR (DMSO-d_6): 7.01–7.03 (8H, d, J = 8.4 Hz, H_8(16), 7.16–7.20 (4H, d, J = 15.6 Hz, H_1(3), 7.41–7.55 (20H, m, H_13), H_1(21)–23), 7.56–7.63 (8H, t, H_7), 7.65–7.67 (8H, d, J = 8.4 Hz, H_8(5,6)), 7.78–7.80 (8H, t, H_6), 8.15–8.18 (8H, d, J = 8.4 Hz, H_5), and 8.75 (4H, s, H_4). 13CAPT-NMR (DMSO-d_6): 134.81 C, 128.21 C, 131.99 C, 127.53 C, 126.20 C, 127.59 C, 127.30 C, 127.39 C, 129.24 C, 129.92 C, 161.10 C, 146.32 C, 131.12 C, 131.25 C, 131.62 C, 146.40 C, 147.33 C, 151.99 C, 128.09 C, 129.74 C, 130.55 C, 130.52 C, and 127.33 C. 2.2.7. Synthesis of BPP-Ant-2 compound

The Synthesis of BPP-Ant-2 was prepared similar to the procedure used in the preparation of BPP-Ant-1 and was prepared using BPP (0.4 g, 0.87 mmol), Ant-2 (1.54 g, 4.34 mmol) and KCO_3 (0.72 g, 5.21 mmol) for 24 h. Yield: 1.28 g (85%). Anal. Calc. for C_{39}H_{44}NO_3P_2: C, 77.46; H, 4.30; N, 2.66. MALDI-MS: m/z calc. 1612.62, found: 1613.45 [M+H]^+ . FT IR (KBr, cm⁻¹): 3008, 3035 and 3048 ν(ν_C-H) 2937 and 2956 ν(ν_C-H). 1643 ν(C-O), 1502, 1577, 1556 and 1624 ν(C= C), 1162, 1179 and 1200 ν(ν_P-O). 948 ν(ν_C-O). 31P NMR (DMSO-d_6): 9.28 (2P, d, P(O-C_2_2H_4)), 24.24 (1P, t, P(O-C_2_2H_4)). H NMR (DMSO-d_6): 7.01–7.03 (8H, d, J = 8.4 Hz, H_8(16), 7.16–7.20 (4H, d, J = 15.6 Hz, H_1(3), 7.41–7.55 (20H, m, H_13), H_1(21)–23), 7.56–7.63 (8H, t, H_7), 7.65–7.67 (8H, d, J = 8.4 Hz, H_8(5,6)), 7.78–7.80 (8H, t, H_6), 8.15–8.18 (8H, d, J = 8.4 Hz, H_5), and 8.75 (4H, s, H_4). 13CAPT-NMR (DMSO-d_6): 134.81 C, 128.21 C, 131.99 C, 127.53 C, 126.20 C, 127.59 C, 127.30 C, 127.39 C, 129.24 C, 129.92 C, 161.10 C, 146.32 C, 131.12 C, 131.25 C, 131.62 C, 146.40 C, 147.33 C, 151.99 C, 128.09 C, 129.74 C, 130.55 C, 130.52 C, and 127.33 C. 2.3. Preparation of graphene-based organophosphazene compounds

The organophosphazene compounds (BPP-Ant-1 and 2, BPP-Ant-1 and 2) was added in water (50 mL) with continuous stirring. And then graphene (5% w/w) was added to the mixture and stirred using a sonicator system for about 0.5 h to allow proper dispersion of graphene inside the mixture. Later, the mixture of organophosphazene compounds (BPP-Ant-1 and 2, BPP-Ant-1 and 2) and graphene nanoplatelet (3 nm) in the water added into the sample cup made from teflon and stirred. The mixture was heated at 180 °C for 8 h with the hydrothermal system under pressure (10 Bar). After cooling the hydrothermal system, the resulting product was filtered off and washed with distilled water and dried for 48 h at 40 °C under vacuum.

3. Results and discussion

3.1. Synthesis and characterization

1-(Anthracene-9-yl)-3-(4-hydroxyphenyl)prop-2-en-1-one (Ant-1) and 1-(anthracene-9-yl)-3-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-one (Ant-2) compounds was obtained according to Claisen-Schmidt condensation method as described in the literature [33,34]. These reactions were obtained from the interactions of 9-acylanthracene with 4-hydroxy-substituted-benzaldehyde in the presence of NaOH (50% solution) in ethanol at room temperature.
cyclotriphosphazene compounds have been obtained as pure. The cene-9-yl)-3-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-one DPP-Ant-2 structure of other compounds was proved by MALDI-MS, elemental analysis, FT-IR, and 1H and 13C NMR spectroscopy methods. The results of the analysis of all compounds are similar procedure, BPP-Ant-1 and BPP-Ant-2 compounds were obtained from the reaction of DPP with 2 equiv. of 1-(anthracene-9-yl)-3-(4-hydroxyphenyl)prop-2-en-1-one (Ant-1) and 1-(anthracene-9-yl)-3-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-one (Ant-2), respectively. The completion of reactions was monitored by TLC. In high yields, di- and tetra-substituted organocyclotriphosphazene compounds have been obtained as pure. The general protocol for the synthesis of anthracene substituted chalcone bearing organocyclotriphosphazenes are shown in Scheme 1.

The structure of Ant-1 and 2 compounds were clarified by elemental analysis, FT-IR, 1H and 13C APT-NMR spectroscopy. The structure of other compounds was proved by MALDI-MS, elemental analysis, FT-IR, 1H, 13C-APT, 31P NMR, and 2D HETCOR NMR spectroscopy methods. The results of the analysis of all compounds are given in detail in the experimental part. Furthermore, the melting points of all compounds were determined by DSC thermal analysis method. The DSC (differential scanning calorimetry) measurements of the compounds were carried out under nitrogen (N2) gas at a heating rate of 10 °C/min. The TGA (thermogravimetric analysis) measurements of the compounds were carried out under nitrogen (N2) gas at a heating rate of 20 °C/min. The thermogravimetric (TGA) analysis measurements made up to 800 °C were investigated. Temperatures at 50% rate degradation for DPP-Ant-1, DPP-Ant-2, BPP-Ant-1, and BPP-Ant-2 compounds were observed at 656, 651, 650 and 630 °C, respectively (Fig. 1). The results obtained show that these phosphazene compounds are thermally

**Scheme 1.** Protocol for synthesis of anthracene substituted chalcone (Ant-1 and 2) bearing organocyclotriphosphazene derivatives: (a) Chalcone: NaOH, EtOH, rt, 10 h; (b) Organophosphazenes: Acetone, K2CO3, reflux, 12–24 h.

**Fig. 1.** The TG curves of anthracene substituted chalcone (Ant-1 and 2) bearing organocyclotriphosphazenes (DPP-Ant-1,2 and BPP-Ant-1,2) heated under nitrogen to 800 °C at a heating rate 10 °C min⁻¹.
stable. The thermal decomposition temperatures of these compounds are summarized in Table 1.

Molecular ion peaks of DPP-Ant-1, DPP-Ant-2, BPP-Ant-1 and BPP-Ant-2 compounds at the mass spectrum obtained by MALDI-MS (Matrix-assisted laser desorption/ionization) technique are observed at 1150.17 m/z, 1210.17 m/z, 1613.45 m/z and 1732.18 m/z and are in agreement with the expected theoretical values. The MALDI-MS spectrum of the DPP-Ant-1 and BPP-Ant-2 compounds are shown, for example, in Fig. 2.

In the structure of Ant-1 and Ant-2 compounds, –OH functional groups which were observed at 3227 and 3393 cm⁻¹, disappeared following chalcone substituted phosphazenes formation, accompanied by the appearance of P–O–C stretching frequencies in the 1225–1285 cm⁻¹ and 1643–1645 cm⁻¹ regions. The peaks between 1643 and 1645 cm⁻¹ are to the chalcone carbonyl (C=O) stretching frequency. The absorption bands in the 3006–3033 cm⁻¹ are to the stretching vibrations of the aromatic CH groups. The P=N stretching vibration peaks, which are observed between 1158 and 1228 cm⁻¹ as strong bands are characteristic peaks of organocyclotriphosphazenes.

The DPP-Ant-1, DPP-Ant-2, BPP-Ant-1, and BPP-Ant-2 compounds have in AB₂ spin system. There are two peaks in the 3¹P NMR spectra of DPP-Ant-1, DPP-Ant-2, BPP-Ant-1, and BPP-Ant-2. The 3¹P NMR spectra of DPP derivatives was observed at δ = 9.60 (1P, t) and 25.26 (2P, d) ppm for DPP-Ant-1, at δ = 11.12 (1P, t) and 24.84 (2P, d) ppm for DPP-Ant-2 in a triplet-doublet. The 3¹P NMR spectra of BPP derivatives was observed at δ = 9.28 (2P, d) and 24.24 (1P, t) ppm for BPP-Ant-1, at δ = 9.70 (2P, d) and 24.75 (1P, t) ppm for BPP-Ant-2 in a doublet-triplet. The 3¹P NMR spectra of DPP, BPP, DPP-Ant-1, and BPP-Ant-2 are depicted in Fig. 3 (a) and (b).

The ¹H and ¹³C APT-NMR spectra for DPP-Ant-1, DPP-Ant-2, BPP-Ant-1, and BPP-Ant-2 are detailed the experimental section. The ¹H, ¹³C APT-NMR NMR spectra of the DPP-Ant-1 is shown, for example, in Fig. 4.

### 3.2. Dielectric and electrical behaviors of organocyclotriphosphazene compounds and their graphene-based composites

The organocyclotriphosphazene compounds (BPP-Ant-1 and 2, DPP-Ant-1 and 2) used in the experiments were first formed with pure state and then composite with nanographene. The use of an impedance analyzer is a method for measuring the dielectric constants of solid materials. In this method, the measurement of the dielectric constants of solid materials is based on the values of C (capacitance) and D (loss factor).

The dielectric constant and dielectric loss factor of the cyclotriphosphazene compounds placed in the disc and the graphene composites of these compounds were calculated by the following equations (1) and (2) [35–37]. During these analyzes, firstly each sample was weighed as 0.1 g, 5 tons of pressure was applied and pelletized in a cylindrical shape with a diameter of 13 mm. Each composition prepared was pelletized to 13 mm in the same conditions and its dielectric properties were measured and compared to the pure states of the organocyclotriphosphazene compounds.

The dielectric properties of the pure states of the compounds were investigated against increasing frequency (from 100 Hz to 20 kHz) and frequencies (at 298 K, 318 K, 338 K, 348 K). The measurements were examined up to 75 °C and compared. It was then observed that the results obtained after this temperature increase were very close.

### Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Td/C</th>
<th>Tg/°C</th>
<th>% Remaining at 800 °C</th>
</tr>
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<tbody>
<tr>
<td>DPP-Ant-1</td>
<td>322</td>
<td>656</td>
<td>27</td>
</tr>
<tr>
<td>DPP-Ant-2</td>
<td>354</td>
<td>651</td>
<td>35</td>
</tr>
<tr>
<td>BPP-Ant-1</td>
<td>322</td>
<td>650</td>
<td>21</td>
</tr>
<tr>
<td>BPP-Ant-2</td>
<td>349</td>
<td>630</td>
<td>18</td>
</tr>
</tbody>
</table>

* a Initial decomposition temperature.
* b Decomposition temperature at 50% mass loss.

![Fig. 2. Positive ion and linear mode MALDI TOF-MS spectrum of (a) DPP-Ant-1 and (b) BPP-Ant-2 was obtained in 1,8-anthracenetrioil (20 mg/mL THF) MALDI matrix using nitrogen laser accumulating 50 laser shots.](image1)

![Fig. 3. 3¹P NMR spectra of compounds; (a) DPP, (b) BPP, (c) DPP-Ant-1, (d) BPP-Ant-2.](image2)

\[
e' = \frac{C_p}{\varepsilon_{0} A_0} \tag{1}
\]

\[
e'' = \varepsilon' \Delta F \tag{2}
\]

where \(\varepsilon'\) is dielectric constant, \(\varepsilon_{0}\) is the dielectric constant of vacuum (8.854 \times 10⁻¹²), \(d\) is the thickness (m) and \(A\) is the effective area (m²) of the sample and \(C\) is the capacitance (F) of the test device.

And then the AC conductivity was calculated below equation [3].

\[
\sigma = \frac{C_p}{\varepsilon_{0} A} \tag{3}
\]

where \(\sigma\) is ac conductivity, \(d\) is the thickness (m) and \(A\) is the effective area (m²) of the sample.

The measured dielectric constant, dielectric loss and AC conductivity results of BPP-Ant-1 and 2, DPP-Ant-1 and 2 against increasing temperature (at 298 K, 318 K, 338 K, 348 K) and frequency (from 100 Hz to 20 kHz) were compared in the Figs. 5–8.

It was determined that the max suitable temperature is 75 °C for...
Fig. 4. $^1$H and $^{13}$C-APT NMR spectra of DPP-Ant-1: (a) $^1$H NMR, (b) $^{13}$C-APT NMR.
the conducted experiments considering the physical behavior (stretching, stretching, softening, breaking, etc.) of the pellets prepared for dielectric measurements against increasing temperature. That is why the maximum temperature was applied at 75°C in the dielectric analysis.

According to the results obtained, the dielectric constant is highest at 75°C against increasing frequency. The dielectric constant increases with increasing temperature while decreasing with increasing frequency. Dipoles mobilization, although depending on the softness of the material, the dipoles in the polymer or material shows a tendency to orient the direction of the applied field [38]. These changes are observed especially at low-frequency values (100–1000 Hz). It also remains constant at high frequencies unchanged. The reason for these results is that the presence of polar groups on the structure increases the dielectric constant [39]. The carbonyl group and conjugation which is bonded to chalcone groups made dielectric constant higher compared to different compounds [40]. The changes in the dielectric constants of the pure states of the compounds are shown comparatively in Fig. 5. In Fig. 6 dielectric loss factors of chalcone containing organocyclotriphosphazenes (BPP-Ant-1 and 2, DPP-Ant-1 and 2) were reduced against increasing frequencies values. Decreasing of the dielectric loss factors proved that the existence of surface polarization in these compounds (BPP-Ant-1 and 2, DPP-Ant-1 and 2) at increased frequencies.

The AC conductivity results of BPP-Ant-1 and 2, DPP-Ant-1 and 2 were given in Fig. 7. The AC conductivity of BPP-Ant-1 and 2, DPP-Ant-1 and 2 were increased with raising frequencies. The rapid rise of AC (alternating-current) conductivity in the low frequencies remains constant at the higher frequencies. The $\varepsilon'$ and $\varepsilon''$ and AC conductivity results of BPP-Ant-1 and 2, DPP-Ant-1 and 2 in the frequency of 1 kHz and at 25°C are shown in Table 2 and compared in Fig. 7.

Dielectric properties of phosphazene composites prepared by doping with nanographene have been investigated against increasing frequency at room temperature. Nanographene addition to all composites made an increase in the real part of permittivity due to the interaction between dipoles of nanographene flakes and $\pi$ bonds of anthracene. As a result of this interaction, BPP-Ant-2/ nanographene composites possess higher $\varepsilon'$ values to compare other composites regarding with the whole range of frequency.

Besides above-mentioned measurements, the DC conductivity of the composites at constant voltage (2 V) was evaluated against increasing temperature.

The change in dc conductivity which was operating in an oven at room temperature and with a heating rate of 10°C/min up to 75°C was examined. DC conductivity value increases linearly with increasing temperature and this is an important evidence that the composite prepared with 2% (w/w) nanographene is a semiconductor. The reason for choosing 2% (w/w) nanographene by weight is due to the fact that the expected conductivity increase in the organophosphazene/nanographene composites which were prepared by 0.5% and 1% by weight from the nanographene for pre-tests did not occur.

As shown in Figure, the increase in the electrical conductivity against the increase in temperature caused by the high aspect ratio of nanographene sheets and their homogeneous dispersion in matrix. The conductivities of other composites are summarized in Table 2. In Table 2 the conductivity versus 1000/T for BPP-Ant-1 and 2, DPP-Ant-1 and 2, BPP-Ant-1 and 2, DPP-Ant-1 and 2 nanographene composites was given. The value of activation energy, $E_a$ of composites is calculated by the given equation (4):

$$\sigma(T) = \sigma_0 \exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

where $\Delta E_a$ is the activation energy, $k_B$ is the Boltzmann constant and $\sigma_0$, the pre-exponential factor. The value of $1.3806 \times 10^{-23}$ J/K is the Boltzmann’s constant ($k_B$), T, which is the absolute temperature. In practice, the $E_a$ is taken to be the slope of an Arrhenius plot of $\ln \sigma$ versus $1/T$ [41]. The slope is equal to $-\Delta E_a/k_B$. The activation energy ($E_a$) is calculated as $E_a = -k_B \times $ slope. Then, a positive value of activation energy using the slope being negative of Arrhenius plots for BPP-Ant-1 and 2, DPP-Ant-1 and 2 nanographene composites are estimated. $E_a$ values of BPP-Ant-1 and 2, DPP-Ant-1 and 2 calculated by equation (4) which are 0.878 eV, 0.638 eV, 0.377 eV and 0.334 eV, respectively (Table 3). When considering these values, there might be more than one possible conduction mechanism regarding to nanographene concentration in the host material according to Jonscher [42] that the $E_a$ values less than 0.8 eV would be a conduction mechanism, on the other hand, the $E_a$ values more than 0.8 eV would be considered as ionic transport [43]. In this case, the ionic conduction is explained by...
high $E_a$ values and low mobility while electronic conduction is characterized by relatively high mobility and lower $E_a$ value.

4. Conclusion

In conclusion, new di-spiro and tetra-spiro organophosphazene compounds (DPP-Ant-1 and 2, BPP-Ant-1 and 2) were synthesized by interaction with conjugate anthracene-substituted...
chalcone compounds (Ant-1 and 2) with organocyclotriphosphazene compounds DPP and BPP. All the compounds were fully characterized and confirmed by elemental analysis, spectroscopic and thermal techniques such as DSC, TGA, mass, FT-IR, $^{1}H$, $^{13}C$-APT, $^{31}P$ NMR and 2D HETCOR NMR. The phosphazene/graphene nanocomposites were obtained by doped with nanographene of these synthesized compounds at %2 (w/w) ratios using BPP-Ant-1,2/nanographene (BPP-Ant-1 and 2, DPP-Ant-1 and 2) cyclotriphosphazene/nanographene composites were reported.

The pure forms of organocyclophosphazenes and the dielectric properties of 2% (w/w) nanographene doped composites are summarized in Table 2. A significant increase was observed in these properties with the contribution of 2% (w/w) nanographene. For compound BPP-Ant-2, the dielectric constant, the dielectric loss and the ac conductivity value increased from 5.86 to 28.57, from 0.015 to 3105, and from $3.63 \times 10^{-9}$ S/cm to $1.72 \times 10^{-6}$ S/cm, respectively. As a result, nanographene doped material has gained semi-conductive properties that are understood by the dc conductivity results measured against the temperature. In Fig. 9, the DC conductivity value increased with the increase in temperature at constant voltage (2 V). As a result, they have been found that graphene-doped phosphazene composites gained semi-conductivity. These properties make graphene/phosphazene composites possible material for optoelectronic and other related applications.

### Table 2

<table>
<thead>
<tr>
<th>Nanographene composites %2 (w/w)</th>
<th>slope</th>
<th>k</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP-Ant-1</td>
<td>10.21</td>
<td>0.086</td>
<td>0.878</td>
</tr>
<tr>
<td>DPP-Ant-2</td>
<td>7.42</td>
<td>0.086</td>
<td>0.638</td>
</tr>
<tr>
<td>BPP-Ant-1</td>
<td>4.39</td>
<td>0.086</td>
<td>0.377</td>
</tr>
<tr>
<td>BPP-Ant-2</td>
<td>3.89</td>
<td>0.086</td>
<td>0.334</td>
</tr>
</tbody>
</table>

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### References