

Research paper

Eu⁺³-doped chalcone substituted cyclotriphosphazenes: Synthesis, characterizations, thermal and dielectrical properties

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ABSTRACT

A series of new cyclotriphosphazene derivatives (**2a–e**) were prepared from the reactions of substituted chalcone compounds (**1a–e**) containing different organic side groups at *para* position with cyclotriphosphazene (**2**) bearing dioxybiphenyl. The structures of **2a–e** were approved by microanalysis and spectroscopic techniques (MS, FT-IR, ³¹P, ¹H, ¹³C, and ¹³C-APT NMR). The thermal behaviors of compounds **2a–e** were investigated by thermogravimetric analysis (TGA). These compounds were found to be stable up to about 300 °C. Dielectric properties of **2a–e** were measured against temperature (between 25 and 160 °C at 1 kHz) and frequency (range from 100 Hz to 5 kHz at 25 °C) using means of an impedance analyzer. Among them dielectric properties of methoxy substituted cyclotriphosphazene **2e** were found to be higher than other phosphazenes. The compound **2b**, which has the lower dielectric property values than other phosphazenes, was selected to determine the influence of Eu⁺³-doping on the dielectric properties of phosphazenes and doped with Eu⁺³ at different mole ratios. At the dielectric properties of Eu⁺³-doped compound **2b** (with increasing molar ratios of Eu⁺³) was observed an excellent increasing according to Eu⁺³-undoped phosphazene compounds.

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1. Introduction

Cyclotriphosphazenes are among the most vigorously researched inorganic cyclic materials. Phosphazenes are compounds that contain phosphorus–nitrogen double bonds, generally four-coordinate quinque-valent phosphorus, although systems with the less common three-coordinate quinque-valent and two-coordinate trivalent phosphorus have also been observed [1–4]. The versatility of substituents that may be placed on both the cyclic and macromolecular backbone has made these systems particularly useful in a variety of applications [4]. For this reason, cyclotriphosphazenes have many potential applications as: dielectric materials [5–8], flame-retardant additives [9,10], fluorescence materials [11,12], clathrates for stereoregulated free-radical polymerizations [13,14], photoinitiators for radical polymerization [15], liquid crystals [16], anti-HIV, antimicrobial, antibacterial and anticancer activity [17–21].

Chalconoids, also known as chalcones, are natural flavonoids related to chalcone. Chalcones are aromatic ketones with two phenyl rings that are also intermediates in the synthesis of many biological compounds. Chalcones can be synthesized by Claisen–Schmidt condensation of benzaldehyde derivatives with acetophenone

compounds in the presence of sodium/potassium hydroxide or as a catalyst [22,23]. Benzylideneacetophenone is the main member of the chalcone derivatives. The different names given to chalcone are β-phenylacrylophenone, phenyl styryl ketone, benzalacetophenone, propylene and α-phenyl-β-benzoyl ethylene [24]. Chalcone compounds have many potential applications as: optical and fluorescence materials [25,26], dielectric devices [27,28], anti-HIV activity [29], antibacterial activity [30] and anti-cancer activities [31–33].

Dielectric constant, dielectric loss factors and conductivity properties of various compounds have been reported by in the literature [8,34–36]. These properties are one of the most common techniques of evaluating solid materials. So, the dielectric constant and loss factor are very important parameters required in the design of devices and moreover, they bring to light much data on the physical or chemical condition of the materials. The dielectric behaviors of compounds are figured out by the charge distribution and the statistical thermal behavior of its polar groups [37]. These dielectric parameters have many potential application areas as materials in multifunctional electronic and optoelectronic devices [38–41]. According to studies in the literature, at the dielectric properties of Eu⁺³-doped materials was observed a significant increasing and the conductive metal composites have gained importance because of they have the potential application areas as materials anti-static materials, self-regulating heater, electro-

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magnetic absorber and preventive of static electricity accumulation [42,43].

In phosphazene chemistry, there are many studies about adamantane, alkoxy-, amino-, thiol and aryloxy substituted phosphazenes [44–48]. However, there are only five articles on the synthesis and characterization of cyclotriphosphazenes containing chalcone compounds as side groups [6,49–52]. Because of the interesting features of chalcone and phosphazene compounds, we designed this study with the aim to resolve this gap in the literature.

Herein, we reported synthesis, characterization and thermal behavior of chalcone substituted-cyclotriphosphazene compounds (**2a-e**). In addition, the dielectric constant, dielectric loss factor and alternating-current (ac) conductivity properties of compounds **2a-e** were determined against temperature (at 1 kHz) and frequency (at 25 °C). Moreover, the dielectric properties of compound **2b**, which has the lower dielectric property values than other compounds, was determined by doped with Eu^{+3} at different mole ratios and compared with other phosphazene compounds.

2. Experimental

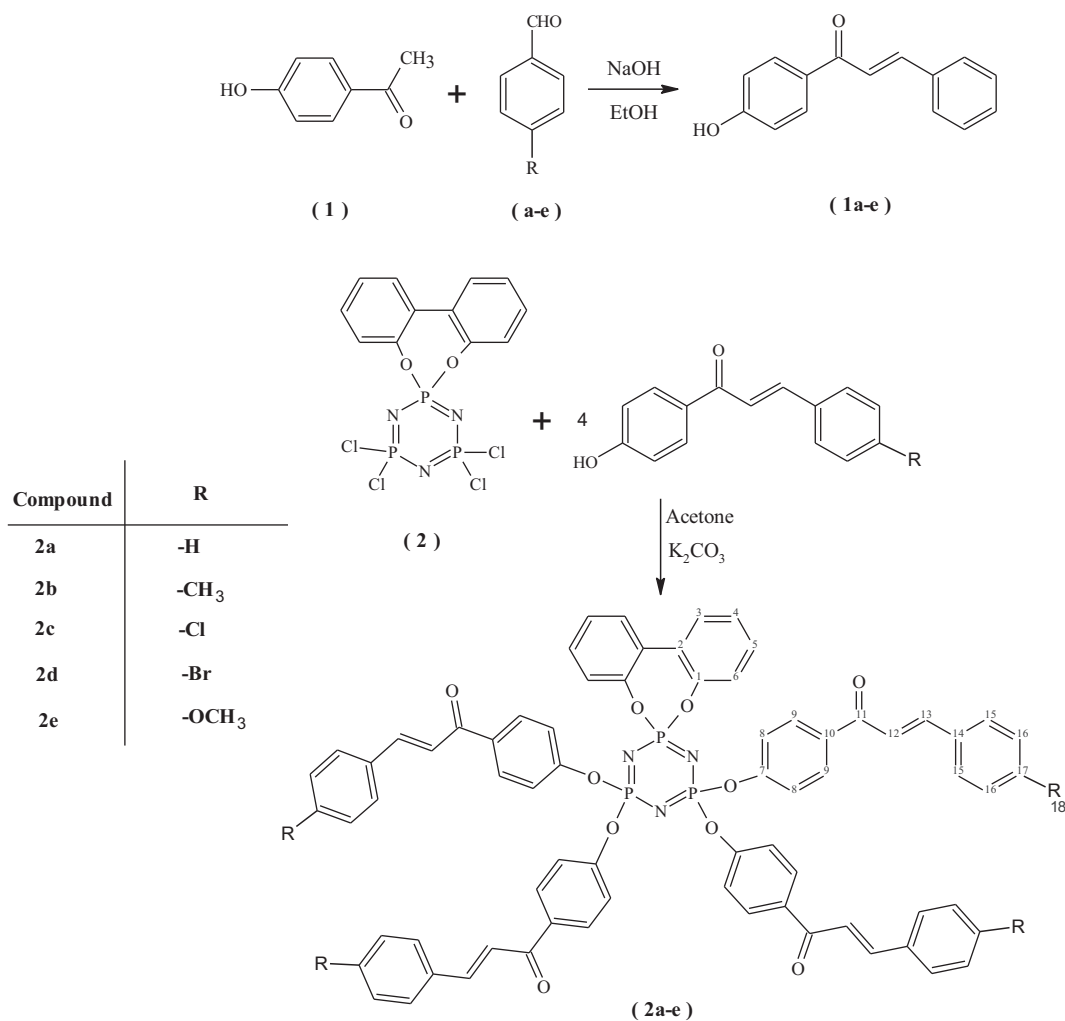
2.1. Materials and method

Benzaldehyde, 4-methylbenzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4-methoxybenzaldehyde, ethanol, acetone,

K_2CO_3 , NaOH and The deuterated solvent (chloroform-d) for NMR analysis were purchased from Merck. Hexachlorocyclotriphosphazene and 2,2'-dioxybiphenyl were recrystallized from petroleum ether and ethanol, respectively. Mass spectra, Microanalysis, ^1H , ^{13}C , ^{31}P NMR and FT-IR spectra were recorded on a Bruker Daltonics microflex mass spectrometer, a LECO 932 CHNS-O apparatus, a Bruker DPX-400 and an Perkin Elmer FT-IR spectrometer, respectively. Thermal analysis of the compounds were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using a TGA-50 thermobalance (20 °C/min) and a SHIMADZU DSC (10 °C/min), respectively. Dielectric measurements were measured at different frequencies and temperatures with a Quad Tech 7600 precision LRC Meter impedance analyzer.

2.2. Synthesis of para-substituted chalcone-cyclotriphosphazene compounds

4'-Hydroxychalcone compounds were obtained by interaction of substituted benzaldehydes with *p*-hydroxyacetophenone [22,23] (Scheme 1). Compound **2** bearing dioxybiphenyl was synthesized and purified as defined by Carriedo et al. [53] (Scheme 1). Detailed procedures were only given compound **2a**. The other compounds containing para substituted chalcone were synthesized and purified by similar reaction procedure.



Scheme 1. Chemical structure and synthetic pathway of **2a-e**.

2.2.1. Synthesis of 3,3,5,5-tetra(4'-oxychalcone)-1,1-bis[spiro(2',2''-dioxo-1'-1''-biphenyl)]cyclotriphosphazene (**2a**)

Compound **2** (1 g, 2.17 mmol) was dissolved in dry acetone (50 mL) under argon atmosphere. And then excess of dry powdered K_2CO_3 (1.8 g, 13.02 mmol) added. The reaction mixture was slowly added, over 0.5 h, to a solution of 4'-hydroxychalcone (**1a**) (2 g, 8.9 mmol) in 20 mL acetone at 0 °C and then refluxed overnight. The reaction followed by thin layer chromatography. After stopping the reaction, the residue was removed by filtration from qualitative filter paper. Acetone was evaporated under reduced pressure (until 15 mL). The mixture was poured into 5% NaOH solution (300 mL). The solid was filtered and washed with distilled water to pH neutral. The solid was dissolved in chloroform and again precipitated in n-hexane and then the solid filtered and dried. Compound **2a** was obtained as a white solid. Yield: 2.1 g (80%). DSC (10 °C/min): 149–150 °C. MALDI-MS: *m/z* calc. 1212.12; found; 1213.87 [M+H]⁺. Microanalysis: (Found: C 71.42, H 4.39, N 3.55%, $C_{72}H_{52}N_3O_{10}P_3$ (1212.12) requires C 71.34, H 4.32, N 3.47%). FT-IR (KBr) ν_{max} (cm⁻¹): 3021 and 3060 ν_{Ar-CH} , 2928 $\nu_{Aliphatic-CH}$, 1667 $\nu_{C=O}$, 1501, 1575, 1596 and 1610 $\nu_{C=C}$, 1179 and 1209 $\nu_{P=N}$, 956 ν_{P-O-C} . ³¹P NMR (400 MHz, CDCl₃) δ = 8.91 (d, 2P, PB), 24.48 (t, 1P, PA). ¹H NMR (400 MHz, CDCl₃) δ = 6.79 (dd, *J* = 4 Hz, 2H, Ar-H⁶), 7.32 (d, *J* = 12 Hz, 8H, Ar-H⁸), 7.37–7.39 (m, 4H, Ar-H³ and H⁵), 7.43–7.45 (m, 10H, Ar-H⁴ and H⁵), 7.51–7.55 (m, 5H, H¹² and Ar-H¹⁷), 7.66 (dd, *J* = 4 Hz, 8H, Ar-H¹⁶), 7.79 (d, *J* = 16 Hz, 4H, H¹³), 8.05 (d, *J* = 12 Hz, 8H, Ar-H⁹). ¹³C NMR (400 MHz, CDCl₃) δ = 147.67 Ar-C¹ (P-O-C), 128.53 Ar-C², 129.94 Ar-C³, 126.41 Ar-C⁴, 129.78 Ar-C⁵, 121.60 Ar-C⁶, 153.83 Ar-C⁷ (P-O-C), 121.22 Ar-C⁸, 130.73 Ar-C⁹, 135.55 Ar-C¹⁰, 188.94 C¹¹ (C=O), 121.31 C¹² (CH=CH), 145.33 C¹³ (CH=CH), 134.70 Ar-C¹⁴, 128.64 Ar-C¹⁵, 128.98 Ar-C¹⁶, 130.42 Ar-C¹⁷.

2.2.2. Synthesis of 3,3,5,5-tetra(4'-oxy-p-methylchalcone)-1,1-bis[spiro(2',2''-dioxo-1'-1''-biphenyl)]cyclotriphosphazene (**2b**)

Compound **1b** (2.12 g, 8.9 mmol). A white solid, Yield: 2.09 g (76%). DSC (10 °C/min): 189–190 °C. MALDI-MS: *m/z* calc. 1268.23; found; 1269.58 [M+H]⁺. Microanalysis: Found: C 72.05, H 4.84, N 3.37%, $C_{76}H_{60}N_3O_{10}P_3$ (1268) requires C 71.98, H 4.77, N 3.31%. FT-IR (KBr) ν_{max} (cm⁻¹): 3025 and 3054 ν_{Ar-CH} , 2919 $\nu_{Aliphatic-CH}$, 1662 $\nu_{C=O}$, 1501, 1568, 1602 and 1630 $\nu_{C=C}$, 1176 and 1201 $\nu_{P=N}$, 942 ν_{P-O-C} . ³¹P NMR (400 MHz, CDCl₃) δ = 8.93 (d, 2P, PB), 24.50 (t, 1P, PA). ¹H NMR (400 MHz, CDCl₃) δ = 2.42 (s, 12H, H¹⁸), δ = 6.78 (dd, *J* = 4 Hz, 2H, Ar-H⁶), 7.22 (d, *J* = 8 Hz, 8H, Ar-H¹⁶), 7.31 (d, *J* = 12 Hz, 8H, Ar-H⁸), 7.37–7.40 (m, 4H, Ar-H³ and H⁵), 7.50 (d, *J* = 16 Hz, 4H, H¹²), 7.55 (m, 10H, Ar-H⁴ and H⁵), 7.81 (d, *J* = 16 Hz, 4H, H¹³), 8.04 (d, *J* = 12 Hz, 8H, Ar-H⁹). ¹³C

Table 1

TGA data for the decomposition of cyclotriphosphazene compounds.

Compounds	T _i (°C ^a)	T _{50%} (°C ^b)	% Remaining at 900 °C
2a	290	689	14
2b	270	664	7
2c	316	682	12
2d	318	572	0
2e	332	665	0

^a Initial decomposition temperature.

^b Decomposition temperature at 50% mass loss.

NMR (400 MHz, CDCl₃) δ = 147.77 Ar-C¹ (P-O-C), 128.52 Ar-C², 129.94 Ar-C³, 126.39 Ar-C⁴, 129.71 Ar-C⁵, 121.62 Ar-C⁶, 153.75 Ar-C⁷ (P-O-C), 121.18 Ar-C⁸, 130.38 Ar-C⁹, 135.57 Ar-C¹⁰, 188.03 C¹¹ (C=O), 120.32 C¹² (CH=CH), 145.41 C¹³ (CH=CH), Ar-131.99 C¹⁴, 128.68 Ar-C¹⁵, 129.71 Ar-C¹⁶, 141.27 Ar-C¹⁷, 21.61 Ar-C¹⁸.

2.2.3. Synthesis of 3,3,5,5-tetra(4'-oxy-p-chlorochalcone)-1,1-bis[spiro(2',2''-dioxo-1'-1''-biphenyl)]cyclotriphosphazene (**2c**)

Compound **1c** (2.3 g, 8.9 mmol). A white solid, Yield: 2.28 g (78%). DSC (10 °C/min): 180–181 °C. MALDI-MS: *m/z* calc. 1349.9; found; 1350.9 [M+H]⁺. Microanalysis: Found: C 64.26, H 4.03, N 3.25%, $C_{72}H_{48}Cl_4N_3O_{10}P_3$ (1349) requires C 64.06, H 3.58, N 3.11%. FT-IR (KBr) ν_{max} (cm⁻¹): 3065 ν_{Ar-CH} , 2923 and 2956 $\nu_{Aliphatic-CH}$, 1664 $\nu_{C=O}$, 1500, 1566, 1606 and 1635 $\nu_{C=C}$, 1176 and 1208 $\nu_{P=N}$, 950 ν_{P-O-C} . ³¹P NMR (400 MHz, CDCl₃) δ = 8.91 (d, 2P, PB), 24.48 (t, 1P, PA). ¹H NMR (400 MHz, CDCl₃) δ = 6.81 (dd, *J* = 4 Hz, 2H, Ar-H⁶), 7.30 (d, *J* = 12 Hz, 8H, Ar-H⁸), 7.35–7.42 (m, 12H, Ar-H³, H⁵ and H¹⁶), 7.42 (d, *J* = 16 Hz, 4H, H¹²), 7.51–7.58 (m, 10H, Ar-H⁴ and H⁵), 7.75 (d, *J* = 16 Hz, 4H, H¹³), 8.02 (d, *J* = 12 Hz, 8H, Ar-H⁹). ¹³C NMR (400 MHz, CDCl₃) δ = 147.73 Ar-C¹ (P-O-C), 128.50 Ar-C², 129.95 Ar-C³, 126.47 Ar-C⁴, 129.77 Ar-C⁵, 121.56 Ar-C⁶, 153.88 Ar-C⁷ (P-O-C), 121.27 Ar-C⁸, 130.41 Ar-C⁹, 135.23 Ar-C¹⁰, 188.55 C¹¹ (C=O), 121.25 C¹² (CH=CH), 143.81 C¹³ (CH=CH), 133.12 Ar-C¹⁴, 129.27 Ar-C¹⁵, 129.77 Ar-C¹⁶, 136.67 Ar-C¹⁷.

2.2.4. Synthesis of 3,3,5,5-tetra(4'-oxy-p-bromochalcone)-1,1-bis[spiro(2',2''-dioxo-1'-1''-biphenyl)]cyclotriphosphazene (**2d**)

Compound **1d** (2.7 g, 8.9 mmol). A white solid, Yield: 2.55 g (77%). DSC (10 °C/min): 211–212 °C. MALDI-MS: *m/z* calc. 1527.7; found; 1528.8 [M + H]⁺. Microanalysis: Found: C 56.75, H 3.27, N 2.81%, $C_{72}H_{48}Br_4N_3O_{10}P_3$ (1527) requires C 56.61, H 3.17, N 2.75%. FT-IR (KBr) ν_{max} (cm⁻¹): 3064 ν_{Ar-CH} , 2917 and 2961 $\nu_{Aliphatic-CH}$, 1663 $\nu_{C=O}$, 1500, 1562, 1606 and 1635 $\nu_{C=C}$, 1175 and 1209 $\nu_{P=N}$, 951 ν_{P-O-C} . ³¹P NMR (400 MHz, CDCl₃) δ = 8.92 (d, 2P, PB), 24.51 (t, 1P, PA). ¹H NMR (400 MHz, CDCl₃) δ = 6.81 (dd,

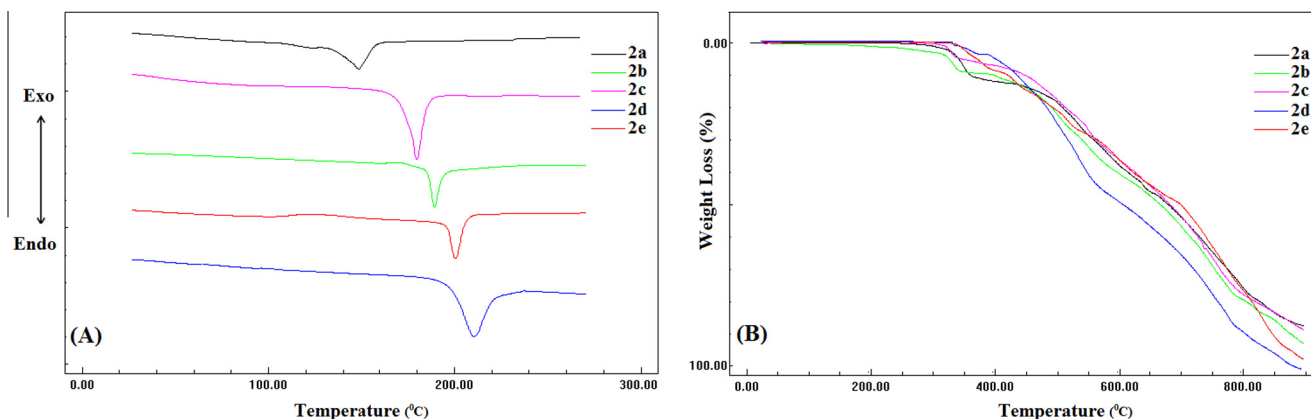


Fig. 1. (A) The DSC curves heated under nitrogen to 300 °C at a heating rate 10 °C min⁻¹ and (B) the TG curves of compounds **2a-e** heated under nitrogen to 900 °C at a heating rate 10 °C min⁻¹.

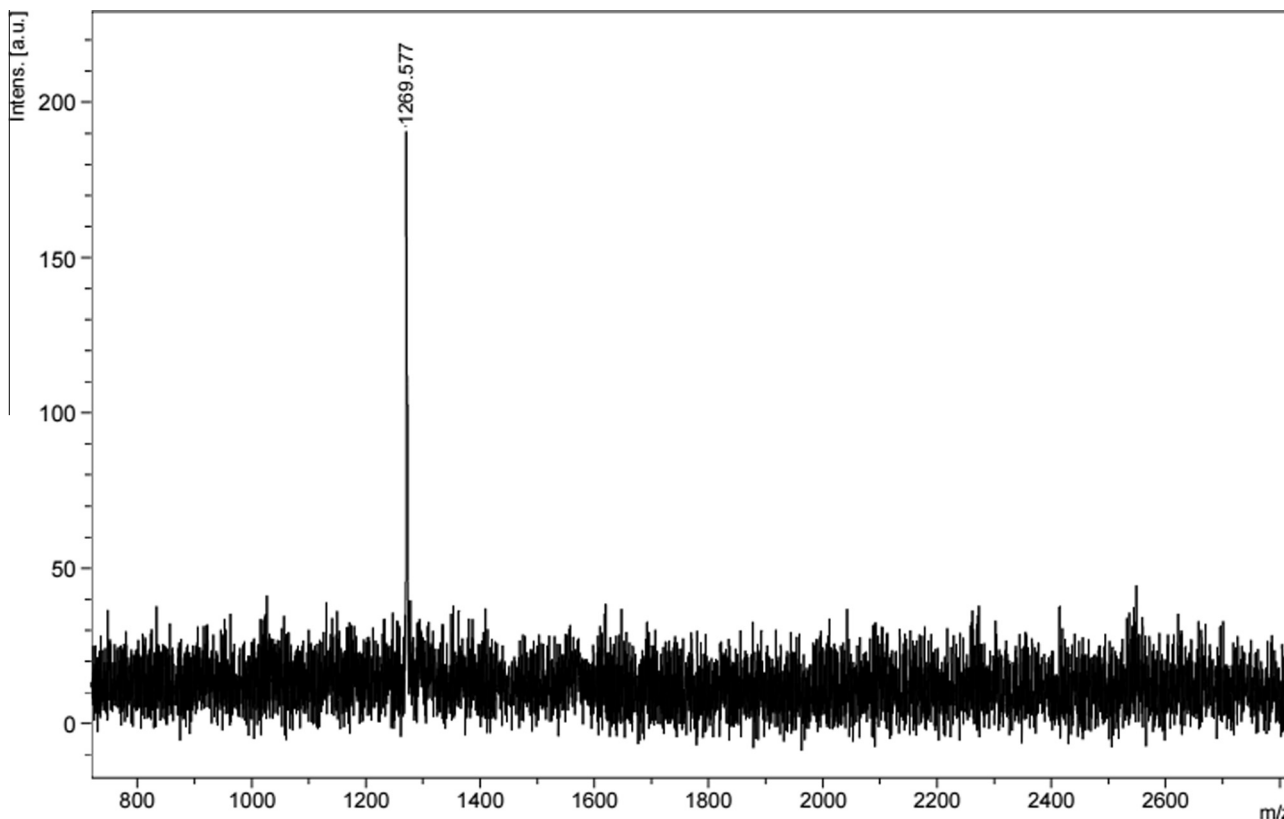


Fig. 2. Positive ion and linear mode MALDI TOF-MS spectrum of compound **2b** was obtained in 1,8,9-anthracenetriol (20 mg/mL THF) MALDI matrix using nitrogen laser accumulating 50 laser shots.

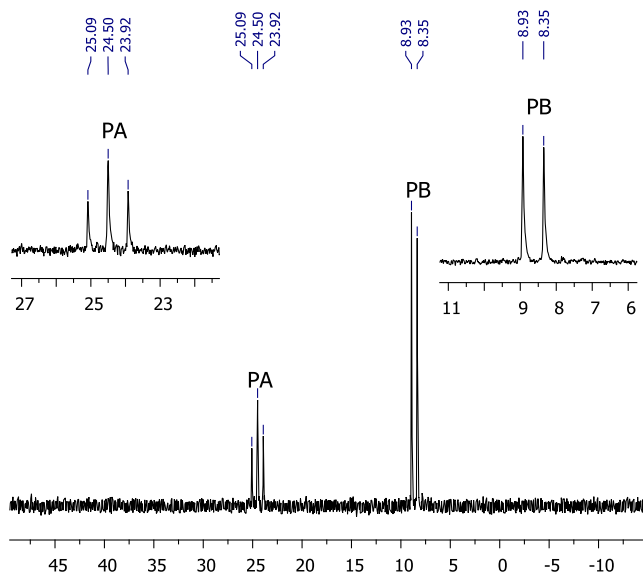


Fig. 3. ^{31}P NMR spectrum of **2b** (chloroform- d).

$J = 4$ Hz, 2H, Ar- H^6), 7.30 (d, $J = 12$ Hz, 8H, Ar- H^8), 7.36–7.39 (m, 4H, Ar- H^3 and H^5), 7.47–7.56 (m, 22H, H^4 , H^{12} , H^{15} and H^{16}), 7.72 (d, $J = 16$ Hz, 4H, H^{13}), 8.02 (d, $J = 12$ Hz, 8H, Ar- H^9). ^{13}C NMR (400 MHz, CDCl_3) $\delta = 147.65$ Ar- C^1 (P–O–C), 128.51 Ar- C^2 , 129.97 Ar- C^3 , 126.48 Ar- C^4 , 129.83 Ar- C^5 , 121.54 Ar- C^6 , 153.90 Ar- C^7 (P–O–C), 121.67 Ar- C^8 , 130.41 Ar- C^9 , 135.23 Ar- C^{10} , 188.50 C^{11} (C=O), 121.26 C^{12} (CH=CH), 143.84 C^{13} (CH=CH), 133.56 Ar- C^{14} , 132.23 Ar- C^{15} , 129.97 Ar- C^{16} , 125.07 Ar- C^{17} .

2.2.5. Synthesis of 3,3,5,5-tetra(4'-oxy-*p*-methoxychalcone)-1,1-bis[spiro(2',2''-dioxo-1'-1''-biphenyl)cyclotriphosfazene (**2e**)

Compound **1e** (2.26 g, 8.9 mmol). A white solid, Yield: 2.45 g (85%). DSC (10 °C/min/): 200–201 °C. MALDI-MS: m/z calc. 1332.22; found: 1333.23 $[\text{M}+\text{H}]^+$. Microanalysis: Found: C 68.62, H 4.61, N 3.22%, $\text{C}_{76}\text{H}_{60}\text{N}_3\text{O}_{14}\text{P}_3$ (1332) requires C 68.52, H 4.54, N 3.15%. FT-IR (KBr) ν_{max} (cm^{-1}): 3064 $\nu_{\text{Ar-CH}}$, 2917 and 2961 $\nu_{\text{Aliphatic-CH}}$, 1663 $\nu_{\text{C=O}}$, 1500, 1562, 1606 and 1635 $\nu_{\text{C=C}}$, 1175 and 1209 $\nu_{\text{P=N}}$, 951 $\nu_{\text{P-O-C}}$. ^{31}P NMR (400 MHz, CDCl_3) $\delta = 8.98$ (d, 2P, PB), 24.57 (t, 1P, PA). ^1H NMR (400 MHz, CDCl_3) $\delta = 3.88$ (s, 12H, H^{18}), 6.79 (dd, $J = 4$ Hz, 2H, Ar- H^6), 6.95 (d, $J = 8$ Hz, 8H, Ar- H^{16}), 7.32 (d, $J = 12$ Hz, 8H, Ar- H^8), 7.34–7.44 (m, 8H, H^3 , H^5 and H^{12}), 7.55–7.61 (m, 10H, Ar- H^4 and H^{15}), 7.79 (d, $J = 16$ Hz, 4H, H^{13}), 8.06 (d, $J = 12$ Hz, 8H, Ar- H^9). ^{13}C NMR (400 MHz, CDCl_3) $\delta = 147.69$ Ar- C^1 (P–O–C), 128.52 Ar- C^2 , 129.93 Ar- C^3 , 126.39 Ar- C^4 , 129.73 Ar- C^5 , 121.59 Ar- C^6 , 153.68 Ar- C^7 (P–O–C), 121.16 Ar- C^8 , 130.31 Ar- C^9 , 135.71 Ar- C^{10} , 188.84 C^{11} (C=O), 119.01 C^{12} (CH=CH), 145.14 C^{13} (CH=CH), 130.45 Ar- C^{14} , 127.48 Ar- C^{15} , 114.41 Ar- C^{16} , 161.78 Ar- C^{17} , 55.44 C^{18} (OCH_3).

2.3. Dielectric properties of compounds **2a-e**

2.3.1. Dielectric constant and loss factors

The dielectric properties of Eu^{+3} -doped and undoped tetrasubstituted chalcone-phosphazene compounds (**2a-e**) were measured against temperature and frequency using means of an impedance analyzer. The compound **2b** was doped with Eu^{+3} at different ratios (5, 10, 20 and 40%). For measurement, Eu^{+3} -doped and undoped phosphazene compounds **2a-e** were pelleted at 5 megapascal pressure and then the thicknesses of the prepared pellets were measured. The dielectric parameters (dielectric constant and loss factors) were calculated below Eqs. (1) and (2).

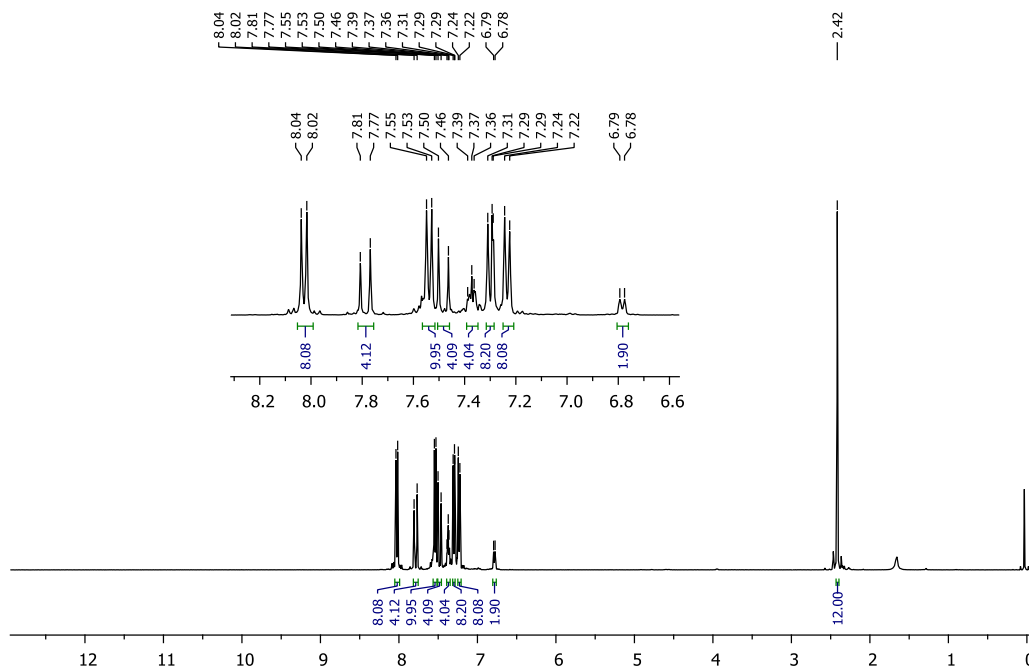


Fig. 4. ^1H NMR spectrum of **2b** (chloroform-d).

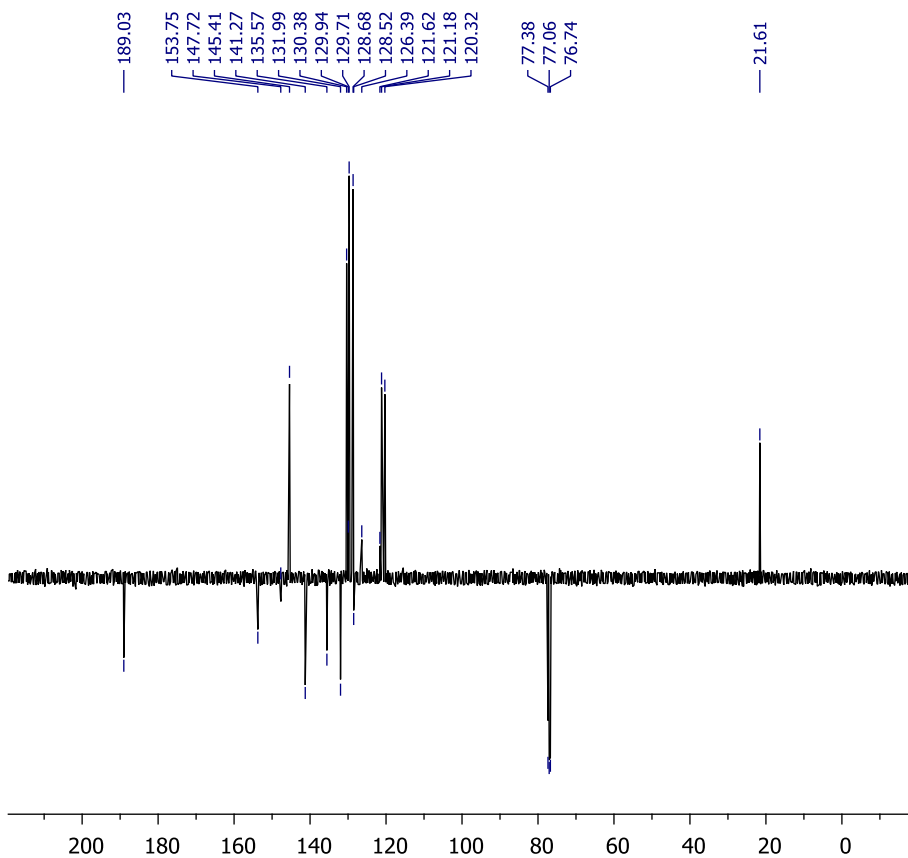


Fig. 5. ^{13}C APT-NMR spectrum of **2b** (chloroform-d).

$$\varepsilon' = C_p \frac{d}{A\varepsilon_0}$$

$$\varepsilon'' = \varepsilon' DF$$

- (1) where ε' is dielectric constant, ε_0 is the dielectric constant of vacuum (8.854×10^{-12}), d is the thickness (m) and A is effective area (m^2) of the sample, ε'' is dielectric loss factors and C is the capacitance (F) of test device.
- (2)

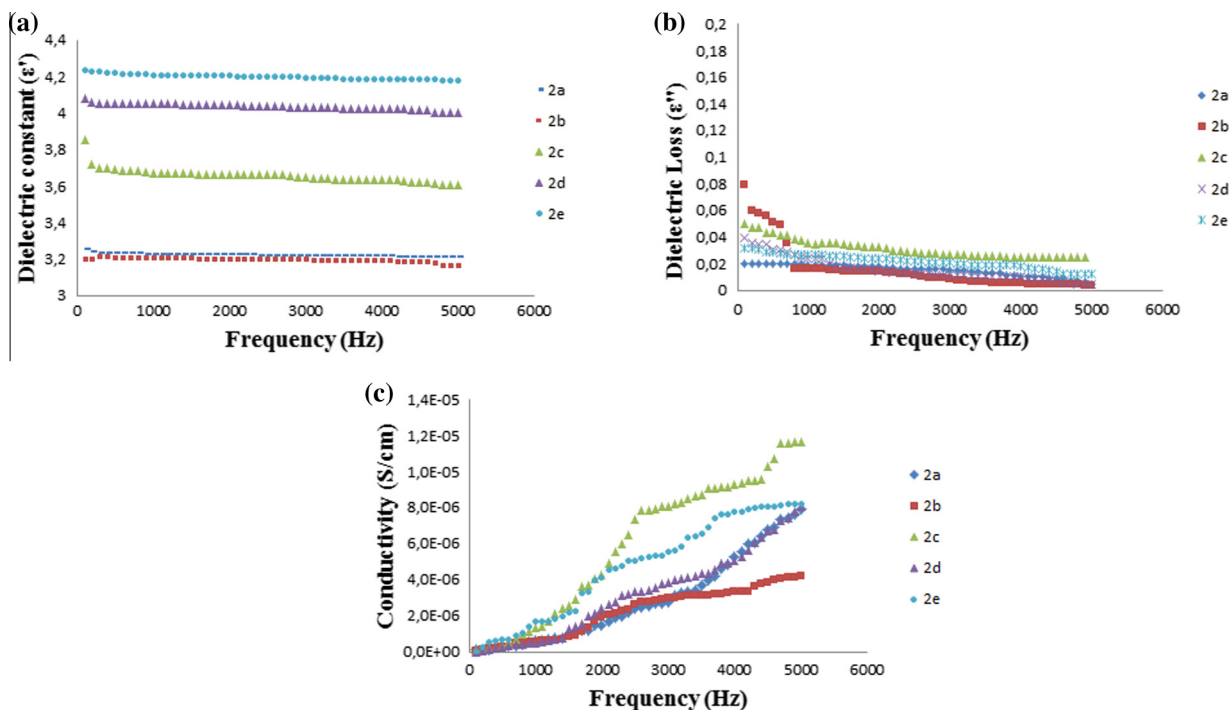


Fig. 6. Variation of dielectric parameters of **2a-e** against frequency; dielectric constants (a), dielectric loss factors (b), and conductivity graphics (c).

2.3.2. Electrical properties

The G_p (conductivity) values of tetrasubstituted chalcone-cyclotriphosphazene compounds (**2a-e**) were measured by impedance analyzer at different frequencies (from 100 Hz up to 5 kHz) and temperatures (range from 25 to 160 °C). And then the electrical conductivity values (AC conductivity) were calculated below Eq. (3).

$$\sigma = G_p \frac{d}{A} \quad (3)$$

where σ is ac conductivity, d is the thickness (m) and A is effective area (m^2) of the sample.

3. Results and discussion

3.1. Synthesis and characterization

Hydroxy chalcone compounds bearing five different side groups at *para* position were synthesized by the interaction of 4-hydroxyacetophenone with benzaldehyde, *p*-methylbenzaldehyde, *p*-chlorobenzaldehyde, *p*-bromobenzaldehyde and *p*-methoxybenzaldehyde, in the presence of NaOH in ethanol, respectively [22,23]. Tetrasubstituted cyclotriphosphazene products (**2a-e**) were normally synthesized in high yields from the reactions of compound **2** with 4.1 equiv. of these hydroxy chalcone compounds (**1a-e**) in the presence of K_2CO_3 in dry acetone. All the reactions followed by TLC. General synthetic presentations and the structures of these compounds are shown in Scheme 1.

The melting points of compounds **2a-e** were determined with differential scanning calorimetry (DSC). In the DSC spectra of compounds **2a-e** were observed a single melting point (Fig. 1). The thermal stability of cyclotriphosphazene compounds were determined by thermo gravimetric analysis methods (TGA-50, 20 °C/min). The starting degradation temperatures of compounds were generally observed between 270 and 332 °C (Fig. 1 and Table 1).

The mass analyses of the chalcone substituted cyclotriphosphazene derivatives were determined by MALDI-TOF-MS technique.

The molecular ion peaks of all the compounds have been given in the experimental section. For example, the molecular ion peak of compound **2b** was observed at 1269.58 (Fig. 2).

When the infrared spectra of chalcone substituted cyclotriphosphazenes (**2a-e**) were investigated, the OH stretching vibration in the structure of compounds **1a-e** was not observed. In similarly, the characteristic stretching vibrations of tetra-substituted chalcone-phosphazene compounds **2a-e** were observed between 945 and 955 cm^{-1} for P–O–C, 1657 and 1666 cm^{-1} for C=O, 1186 and 1193 cm^{-1} for P=N stretching vibrations. In addition, the PCl_2 bands are disappeared.

^{31}P NMR spectra of **2a-e** display the expected AB_2 spin system. As expected, there are one double and one triplet including two peaks at ^{31}P NMR spectra of all the compounds (such as Fig. 3).

In the 1H NMR spectra of compounds **2a-e**, the OH protons of chalcone groups are disappeared. The methyl and methoxy protons for the compounds **2b** (Fig. 4) and **2e** were observed at 2.42 and 3.88 ppm, respectively. The ratio of the protons integral height in the 1H NMR spectrum of the compounds **2a-e** supports the proposed structures.

The locations of carbon peaks of primary, secondary and tertiary carbon atoms were defined by using ^{13}C -APT NMR technique. The carbonyl carbon atoms (C=O) of compounds **2a-e** were observed at 188.94, 189.03, 188.55, 188.50 and 188.84 ppm, respectively. The methyl and methoxy carbons for compounds **2b** (Fig. 5) and **2e** were observed at 21.61 and 55.44 ppm, respectively.

Table 2

The dielectric constant (ϵ') dielectric loss (ϵ'') and ac conductivity (σ) values of **2a-e** in the frequency of 1 kHz and at 25 °C.

Compounds	ϵ'	ϵ''	σ (Siemens/cm)
2a	3.22	0.019	5.84×10^{-7}
2b	3.20	0.015	5.30×10^{-7}
2c	3.67	0.035	1.31×10^{-6}
2d	4.04	0.024	4.69×10^{-7}
2e	4.20	0.026	1.67×10^{-6}

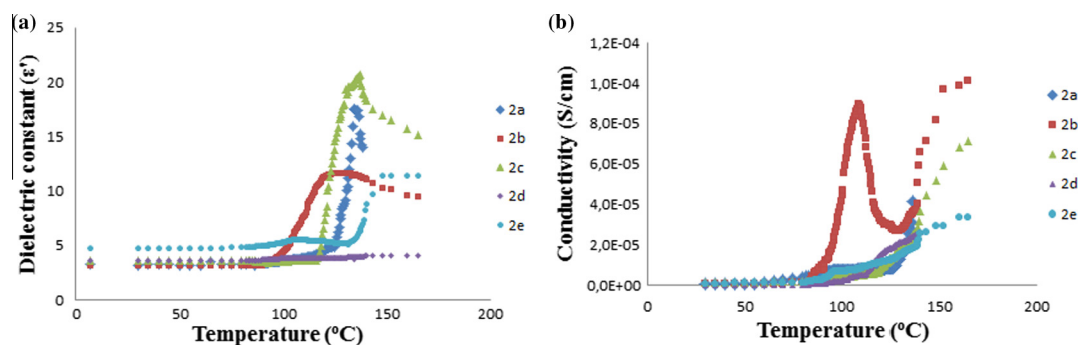


Fig. 7. Variation of dielectric parameters of **2a-e** against temperature ($^{\circ}\text{C}$); dielectric constants (a), and conductivity graphics (b).

3.2. Dielectric behavior

We aimed to investigate the dielectric properties of **2a-e**, which have different organic groups at para position as a function of frequency and temperature. The dielectric parameters (Cp, DF and Gp) of **2a-e** were measured by using impedance analyzer against increasing frequency (from 100 Hz to 5 kHz) and temperature (from 25 to 160 $^{\circ}\text{C}$) and the ϵ' , ϵ'' and σ values were calculated with Eqs. (1–3).

The ϵ' values of all the compounds were decreased towards increasing frequencies. The dielectric constants of **2a-e** were compared in Fig. 6. The compound **2e** containing methoxy group was observed higher dielectric constant (ϵ') value than other compounds. The phenomena implies that free electrons on the oxygen atom in the methoxy group are due to an increase in polarization with conjugation [54]. On the other hand, compound **2b** bearing methyl group showed that has a lower dielectric constant (ϵ') value than other compounds. The ϵ' , ϵ'' , $\log \sigma$ values measured for each

compound in at the frequency (1 kHz) and room temperature are submitted in Table 2.

The ϵ' values of all chalcone structure having phosphazene compounds were observed to increase with increasing temperature Fig. 7. As one of the reasons contributing an increase in dielectric constant which is resulting from temperature increase that is responsible for conversion of the bound charges to the charge carriers which are increasing charge carrier concentration always leads easy sequence of dipoles in the applied AC electrical field. The ϵ' of these materials reached to a maximum height at the value near to the melting points and it did not change after about 150 $^{\circ}\text{C}$. The electrical conductivities of compounds (**2a-e**) increased at high temperatures Fig. 7. The similar results have also been observed in the literature studies [55,56].

The compound **2b**, which has the lower dielectric constant than other phosphazene was selected to determine the influence of Eu^{+3} -doping on the dielectric properties of phosphazenes and doped with Eu^{+3} at different mole ratios. The dielectric properties

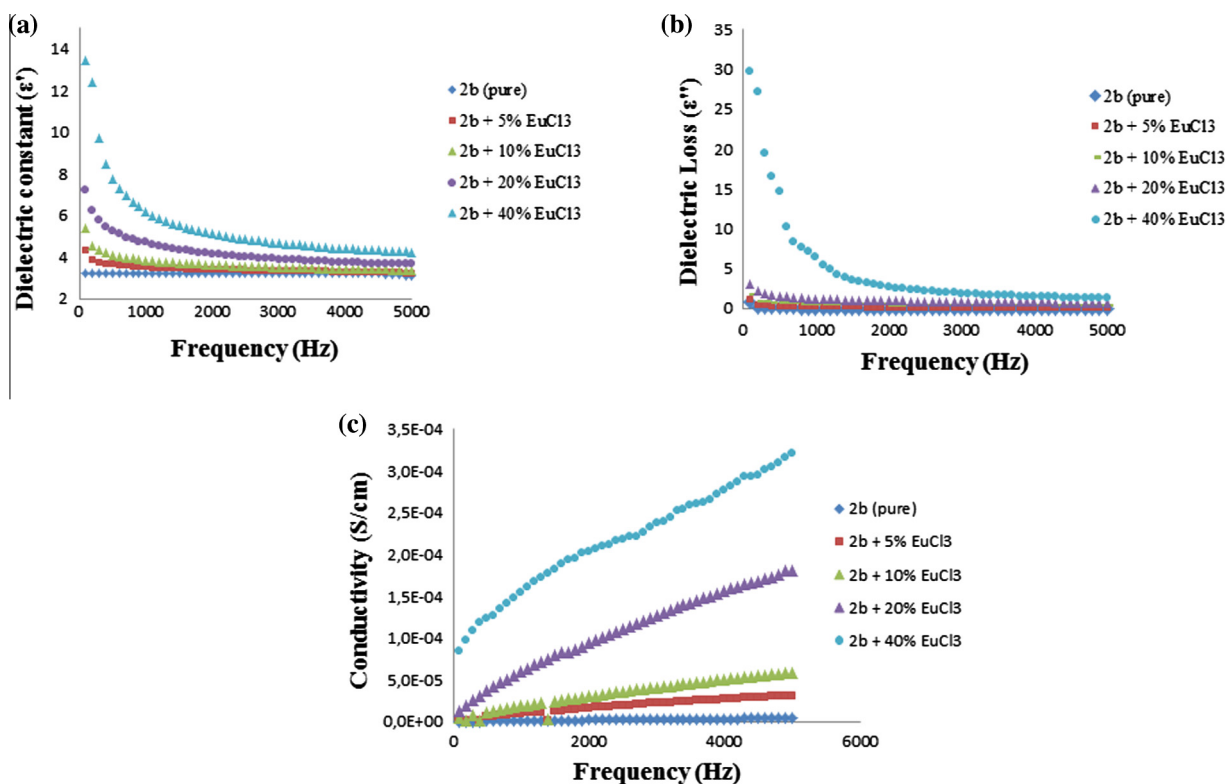


Fig. 8. Variation of dielectric parameters of compound **2b** doped with EuCl_3 at different concentrations; dielectric constants (a), dielectric loss factors (b), and conductivity graphics (c).

Table 3

The dielectric constant (ϵ') dielectric loss (ϵ'') and ac conductivity (σ) values of compound **2b** doped with EuCl_3 at different concentrations in the frequency of 1 kHz and at 25 °C.

Conc.	ϵ'	ϵ''	σ (Siemens/cm)
Pure (2b)	3.20	0.015	5.30×10^{-7}
5% EuCl_3	3.52	0.25	3.12×10^{-6}
10% EuCl_3	3.84	0.48	1.84×10^{-5}
20% EuCl_3	4.73	1.19	5.92×10^{-5}
40% EuCl_3	6.17	6.40	1.44×10^{-4}

of the compounds are changing when the materials are mixed with Eu^{+3} at the different mole ratios. For example, the particles are almost homogeneously distributed in material without interacting with each other at low mole ratios. By contrast, the particles interacting with each other begin to cluster at increasing filler mole ratios. At a certain mole ratio, the growing clusters reach a size that contact with each other and then the conductor forms a network. Hereby, the network formation can be caused to a significant increase in electrical conductivity [57,58].

The dielectric properties of Eu^{+3} -doped compound **2b** (with increasing molar ratios of Eu^{+3}) was observed an significant increasing according to Eu^{+3} -undoped phosphazene compounds. This increase in the dielectric properties is clearly seen in Fig. 8. The reason of this increasing can depend on that has the presence of the load centers in the structure [59]. These centers cause a current conduction under an applied voltage and the formed free electrons cause a current conduction. The ϵ' , ϵ'' , $\log \sigma$ values of **2b**/ EuCl_3 composites at different filler concentration in the frequency (1 kHz) and room temperature are submitted in Table 3.

4. Conclusion

As a result, the new cyclotriphosphazene compounds (**2a-e**) bearing para substituted chalcone compounds (**1a-e**) were designed and synthesized for the first time. The structures of these compounds were confirmed by microanalysis, mass, 1D (^{31}P , ^1H , ^{13}C , ^{13}C -APT) NMR and FT-IR spectroscopy techniques. The dielectric properties of Eu^{+3} -doped (only **2b** against frequency) and undoped compounds prepared in a plate from were tested by means of an impedance analyzer as a function of temperature and frequency given as compared with each other. Eu^{+3} -doped substituted cyclotriphosphazene **2b** have shown that the higher dielectric constant, dielectric loss factors and conductivity values than undoped compound **2b** (at 1 kHz). Other compounds have not been subjected to doping with Eu^{+3} , but it is expected that these compounds most likely shown similar effect on dielectric properties as compound **2b** when doped with Eu^{+3} . Our study suggests that Eu^{+3} -doped substituted phosphazene derivatives promising candidate materials in multifunctional electronic and optoelectronic devices.

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