

# Synthesis and Straightforward Quantification Methods of Imino Nitroxide-Based Hexaradical Architecture on a Cyclotriphosphazene Scaffold

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## Supporting Information

**ABSTRACT:** The synthesis of a homogeneous neutral hexaradical architecture consisting of six imino nitroxide radical moieties covalently bonded on a cyclotriphosphazene scaffold was reported. The synthesis of hexaradical imino nitroxide compounds follows the Ullman procedure involving the condensation of 2,3-bis-(hydroxylamino)-2,3-dimethylbutane with hexa-(4-formylphenoxy)-cyclotriphosphazene (**3**) followed by oxidation of the condensation product hexa-[4-(1-hydroxy-4,4,5,5-tetramethyl-2-imidazoline-2-yl)-phenoxy]cyclotriphosphazene (**2**) by NaIO<sub>4</sub>. Characterization of hexaradical was performed by X-ray and SQUID in solid state and by EPR, absorption spectroscopy, and electrochemistry in solution. CV of **1** shows an oxidation peak at 1.184 V (vs SCE) and a reduction peak at -0.883 V, both characteristics of the presence of phenyl imino nitroxide (**7**) moieties, suggesting that the contribution of the cyclotriphosphazene core is negligible. Attention was particularly focused on developing methods, UV-vis spectroscopy and square-wave voltammetry, to quantify the number of radicals in a way to confirm easily and rapidly the polyradicals' structure.



## INTRODUCTION

Nitroxides are one of the intensely investigated open-shell compounds because of their high stability, ease of synthesis, and rich array of applications such as sensors,<sup>1a</sup> catalysts<sup>1b</sup> for oxidation of alcohols, building blocks<sup>1c</sup> in magnetic materials, and dynamic nuclear polarization (DNP) agents<sup>1d</sup> to enhance NMR signals of dilute samples. Special interest was devoted to the synthesis of dendrimeric multiradicals with nitroxides as end groups with the purpose of spin trapping<sup>2</sup> for nitric oxide and contrasting agents<sup>3</sup> in magnetic resonance imaging (MRI). Among the dendrimeric structures, the cyclotriphosphazene core provides a unique platform to be partially<sup>4–6</sup> or completely<sup>5–9</sup> functionalized by incorporating radical moieties depending on the needs of application. Studies on cyclotriphosphazene core multiradicals were mostly<sup>5–9</sup> devoted to EPR and magnetic analysis. Even if nitroxide radicals are well-known to be redox-active species, no studies filling electrochemical characterization of nitroxide–cyclotriphosphazene hybrid compounds were published yet. However, the electrochemical behaviors of the radical moieties as well as the influence of the scaffold on the potentials are critical points for the development of electrochemical application. Therefore, electrochemical analyses of cyclotriphosphazene-based neutral

hexaradical by comparing with its parent counterpart, phenyl imino nitroxide, were performed to a great extent.

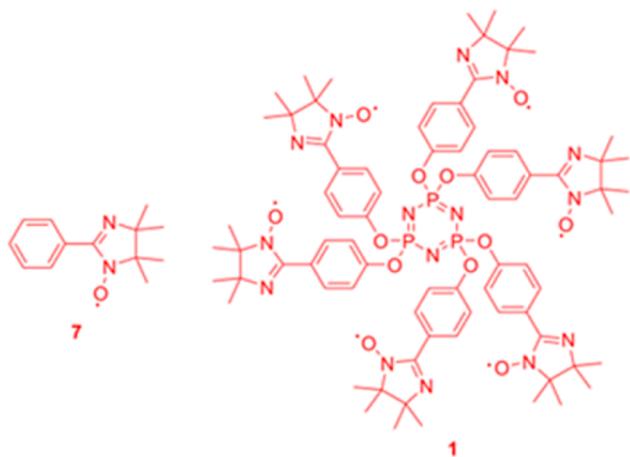
Herein, the controlled synthesis and deep characterization of a polyradical, a cyclotriphosphazene bearing six imino nitroxide radicals (**1**), were reported (see Figure 1). Imino nitroxide was privileged instead of nitronyl nitroxide to be sure of the homogeneity of the radical gender present on the polyradical.

To the best of our knowledge, the quantification of the number of imino nitroxide radicals present on **1** was determined by UV-vis and electrochemistry for the first time, both straightforward and routine available techniques, by comparing with phenyl imino nitroxide (**7**) as a reference standard.

## RESULTS AND DISCUSSION

Hexaaldehyde (**3**) was prepared in 98% yield according to literature<sup>10</sup> slightly modified by using K<sub>2</sub>CO<sub>3</sub>-promoted substitution of hexachlorocyclotriphosphazene (**5**) by 4-hydroxybenzaldehyde (**6**) in anhydrous THF. Stirring reagents damped all at once at room temperature and simple workup as easy as just washing with water and then with Et<sub>2</sub>O gave

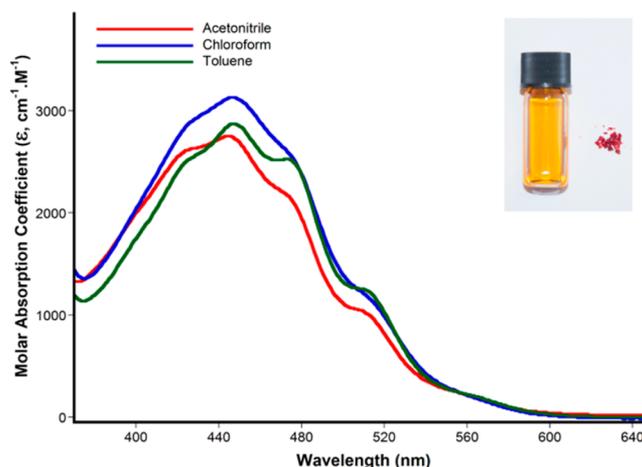
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**Figure 1.** Structures of reference radical **7** and hexaradical **1**.

spectroscopically pure **3** in excellent yield. Using  $K_2CO_3$  rather than  $NaH$ <sup>11</sup> or  $Cs_2CO_3$ <sup>12</sup> as well as no need for phase transfer catalyst<sup>13</sup> made this method a cheaper way. Radical species were synthesized on the basis of Ullman<sup>14</sup> and Tamura<sup>15</sup> protocols (Scheme 1). **3** was reacted with an excess of 2,3-bis(hydroxylamine)-2,3-dimethylbutane<sup>16</sup>(**4**) in the presence of TsOH as catalyst in a minimum of MeOH to yield the radical precursor. The completion of the reaction was monitored by FT-IR following the disappearance of the aldehyde signal at  $1702\text{ cm}^{-1}$ . In general, condensation of an aldehyde with 2,3-bis(hydroxylamine)-2,3-dimethylbutane generates the corresponding 1,3-dihydroxyimidazolidine adduct, but in some cases the dehydration process takes place at elevated temperatures,<sup>17</sup> allowing the formation of 1-hydroxy-2-imidazoline in solution. However, in the present case, dehydration also took place at room temperature and led to the formation of 1-hydroxy-2-imidazoline derivative (**2**) instead of the anticipated 1,3-dihydroxyimidazolidine derivative (**13**). 1-Hydroxy-2-imidazoline derivative (**2**) was isolated, and its structure was

confirmed by MALDI-TOF MS (see Supporting Information,  $m/z$  1540  $[M + 6H]$ ). In the last stage, oxidation of **2** was performed with aqueous  $NaIO_4$  to afford **1**, as an orange solid, in 42% yield (see Figure 2, inset). MALDI-TOF MS using

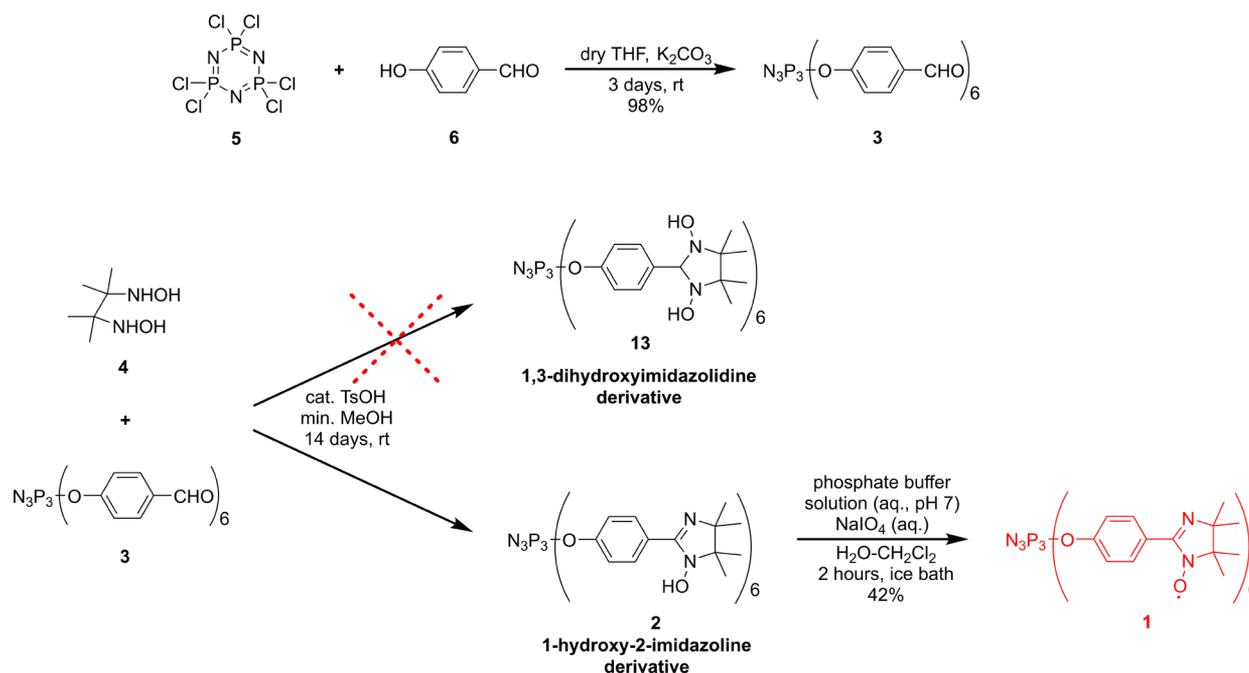


**Figure 2.** UV-vis spectra for  $n \rightarrow \pi^*$  transitions of **1**. Inset:  $10^{-3}\text{ M}$  chloroform solution of **1** and crystals of **1**.

*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile as matrix shows a peak at an  $m/z$  of 1529  $[M^+]$ , which is evidence of the formation of **1**, as well as elemental analyses demonstrate its purity (Supporting Information).

Characteristic features of aromatic imino nitroxides are their colors, from orange to crimson in solid state and orange to red in solution with a broad absorption band accompanying vibronic components in visible region. A typical band around  $\lambda_{\text{max}} \approx 443\text{ nm}$ , intrinsic of the nitroxide fragment, was assigned to  $n \rightarrow \pi^*$  transitions. **1** and **7** were soluble in numerous solvent including acetonitrile, chloroform, and toluene in which the Beer-Lambert Law was observed for both compounds in the

### Scheme 1. Synthetic Route to **1**



B

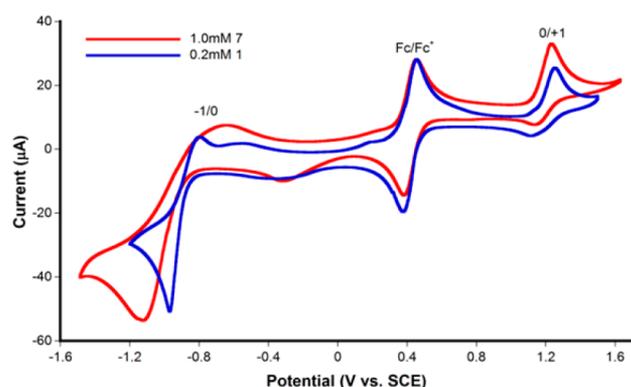
range from  $10^{-5}$  to  $10^{-3}$  M for **7** and from  $10^{-5}$  to  $4.10^{-4}$  M for **1** (Supporting Information). According to molar extinction coefficient ( $\epsilon$ ) values calculated from the radical band centered around 443 nm, a hypochromic effect<sup>18</sup> (representative of the interaction between radical moieties) was not observed for **1**. As a result, the effects due to the cyclotriphosphazene core are negligible, and the molar extinction coefficient ( $\epsilon$ ) of **1** is linearly dependent on the radical number on the scaffold as was already observed for TEMPO moieties.<sup>9</sup> Consequently, simply dividing the  $\epsilon$  of **1** by that of **7** will give us the number of radical moieties present on **1** (Figure 2, Table 1). So, simple and rapid determination of the number of radicals on a polyradical by absorption spectroscopy was successfully demonstrated within the  $\pm 10\%$  tolerance<sup>9</sup> of  $\epsilon$ .

**Table 1.** UV–Vis Data for the  $n-\pi^*$  Transitions of **7** and **1** at Room Temperature<sup>a</sup>

solvent	$\lambda_{\max}$ <b>7</b>	$\epsilon$ <b>7</b>	$\lambda_{\max}$ <b>1</b>	$\epsilon$ <b>1</b>	number of radicals on <b>1</b>
acetonitrile	441	418	444	2751	6.58
chloroform	443	484	447	3129	6.46
toluene	445	442	448	2870	6.49

<sup>a</sup> $\lambda_{\max}$  in nm,  $\epsilon$  in  $\text{cm}^{-1} \text{M}^{-1}$ .

Imino nitroxides are redox-active molecules to be oxidized to oxo-ammonium cation or reduced to aminoxyl anion. Electrochemical behaviors of radical **7** and **1** were investigated by cyclic voltammetry (CV). Reference radical **7** showed a quasi-reversible oxidation wave at 1.183 V vs SCE and a reversible reduction one at  $-0.881$  V. For **1**, oxidation occurred at 1.184 V in a quasi-reversible process, and reduction occurred at  $-0.883$  V in a reversible process. Redox processes of **1** almost overlap with those of phenyl imino nitroxide (**7**) (Figure 3).



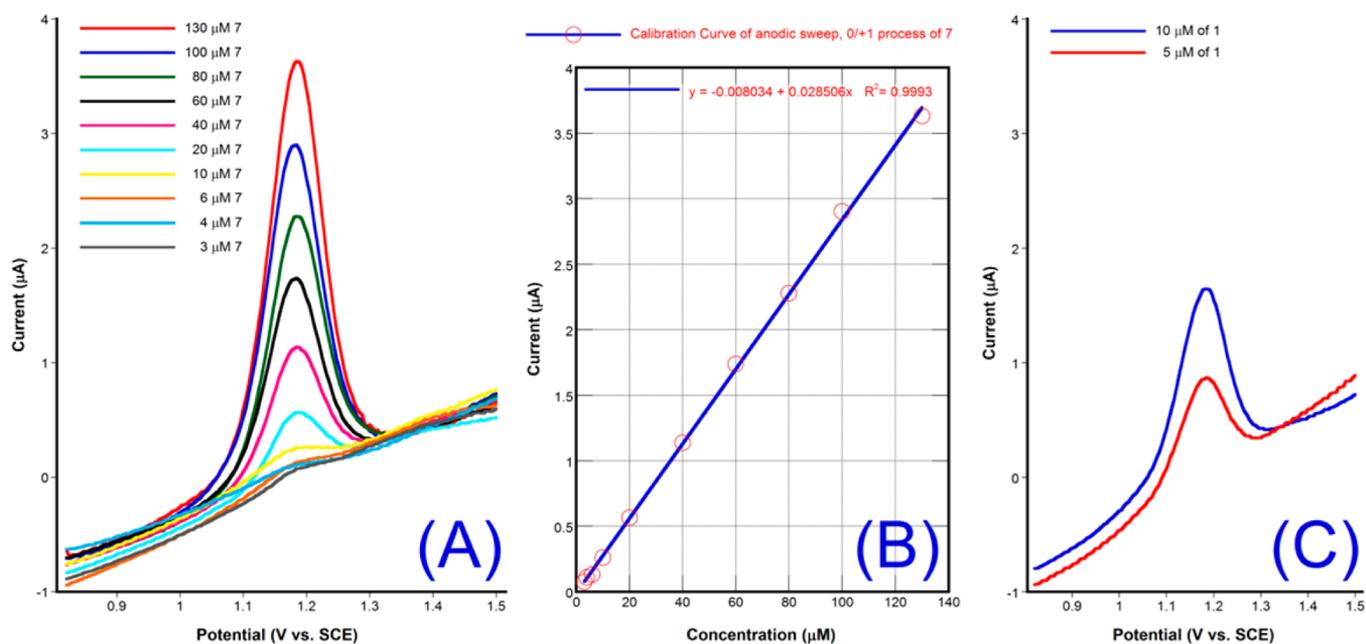
**Figure 3.** Cyclic voltammograms of reference radical **7** and hexaradical **1** recorded at rt in acetonitrile, 0.1 M  $n\text{-Bu}_4\text{BF}_4$  as supporting electrolyte, scan rate of 50 mV/s.

This suggests that cyclotriphosphazene core has almost no influence on the redox potentials of **1**. Redox characteristics and observed potentials of **7** and **1** are in accordance with the literature.<sup>19,20</sup> Square-wave voltammetry (SWV) is a powerful technique<sup>21</sup> for quantification of organic species. To the best of our knowledge, SWV was not utilized for the quantification of imino nitroxides previously. A protocol was established for simple and rapid quantification of INs with a standard SWV run. After optimization of SWV experimental conditions, the oxidation process (0/+1) of ref **7** was studied by anodic sweeping to plot a calibration curve (concentration versus

current), which was linear in the range of 3–130  $\mu\text{M}$  (see Figure 4a and b). Two known concentrations of **1** ( $C_1$ ) then were analyzed under the same conditions. For these known concentrations, a measured current response is obtained ( $I_{\text{measured}}$ ) that corresponds to a theoretical concentration ( $C_{\text{theoretical}}$ ) on the calibration plot of **7**. Simply dividing the  $C_{\text{theoretical}}$  by  $C_1$  allows us to demonstrate that the cyclotriphosphazene scaffold of **1** contains six independent imino nitroxide radicals (Table 2, Figure 4). Consequently, SWV is a simple and straightforward technique to quantify radical moieties on the polyradical.

**1** and **7** were investigated by EPR spectroscopy in  $10^{-4}$  M dichloromethane–toluene (1:1) solutions in the temperature range of 293–123 K. Both spectra showed a seven-line hyperfine pattern typical of imino nitroxide<sup>22</sup> in solution. The spectrum of **7** is in accordance with the literature with an intensity ratio of 1:1:2:1:2:1:1 (Figure 5, inset), whereas the spectrum of **1** presents two main jagged peaks centered at  $g = 2.0026$  separated by ca. 4.20 G due to the sum of at least two superposed different spectra (Figure 5). When the temperature was lowered, the ridges on the spectrum began to shrink and disappeared, so the spectrum changed to a single-narrowed signal<sup>23</sup> (Supporting Information) due to the anisotropic and spin-exchange effects. The spectrum of **1** could be explained in terms of a through-space spin-exchange mechanism between the radicals.<sup>8</sup> The spectrum was simulated on the basis of interconversion of two molecule conformations in solution. In the first conformation, radicals are too far from each other and act as independent radicals (independent form). In the second conformation, three radicals disposed on the same side of the cyclotriphosphazene scaffold are close enough to each other to undergo a strong exchange-interaction independently from the radicals of the other side (interacting form). The best fitting parameters have been obtained for a ratio 2:98 of the aforementioned conformations. Contributions are 2% molar abundance for the independent form with  $a_{\text{N1}} = 9.1$  G,  $a_{\text{N2}} = 4.1$  G,  $\Delta H_{\text{p-p}} = 1.8$  G, and 98% molar abundance for the interacting form with  $a_{\text{N1}} = 3.2$  G,  $a_{\text{N2}} = 1.6$  G, and  $\Delta H_{\text{p-p}} = 6.9$  G.

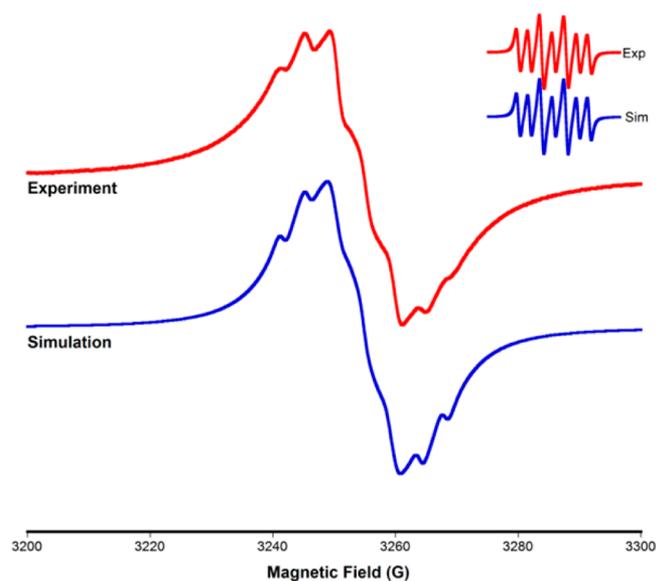
Single crystals of polyradical **1** were obtained from slow evaporation of a mixture of ethyl acetate–toluene–heptane, and the structure was determined by X-ray diffraction. Three radicals are situated above the cyclotriphosphazene core and the three others below (Figure 6). Meaningful bond distances and angles for **1** are reported in Tables 3 and 4, respectively. The P–N and P–O distances as well as the P–N–P and N–P–N angles are in accord with the previous structure of this type.<sup>24</sup> The same results were observed for the C–O distance between the first carbon atom of each phenyl ring and the O atom attached to the P atom of the cyclophosphazene ring. Different data were collected from many crystals obtained from different synthetic batches to determine the structure accurately. However, all attempts resulted in a highly disordered molecular structure. In the first step of the structure determination, it seems that there is a mixture of nitronyl and imino nitroxide radicals. However, in agreement with other characterizations, further refinements show that some imino nitroxides are disordered on two positions in a  $180^\circ$  rotation (head to tail). This is clearly evidenced by free refinement of their oxygen atom of the NO groups that closely reach half occupation. This is what causes the high disorder of the structure because of nonexact superposition of the  $180^\circ$  rotated imino nitroxide moiety. Further confirmation comes from the finding of extra



**Figure 4.** Anodic square-wave voltammetry analyses in 0.1 M  $n\text{-Bu}_4\text{NBF}_4$ /acetonitrile solutions of the radicals: (A) for (0/+1) process of 7; (B) calibration curve for (0/+1) process of 7; and (C) for (0/+1) process of 1.

**Table 2.** Square-Wave Voltammetry (SWV) Analyses of 1

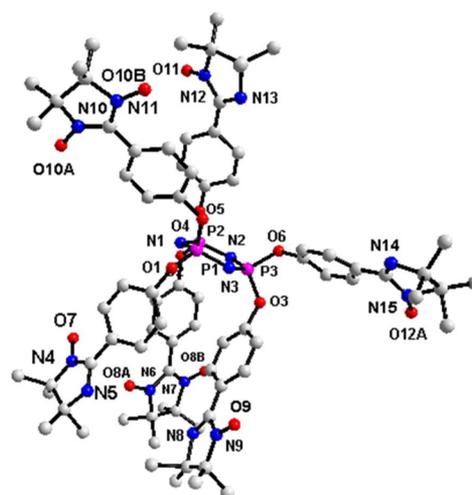
$C_1$ ( $\mu\text{M}$ )	$I_{\text{measured}}$ ( $\mu\text{A}$ )	$C_{\text{theoretical}}$ ( $\mu\text{M}$ )	number of radicals on the scaffold = $C_{\text{theoretical}}/C_1$
10	1.642	56.1	5.61
5	0.869	30.8	6.15



**Figure 5.** X-band EPR spectrum of 1 in dichloromethane–toluene (1:1) solution ( $10^{-4}$  M) at 253 K and its simulation. Inset: EPR spectrum of 7 at the same conditions and its simulation.

electron density, which was attributed to one toluene molecule on the 2 axis and disorder on two positions in a head-to-tail configuration as well (see Figures S34 and S35).

At room temperature, the product of the magnetic susceptibility with temperature ( $\chi T$ ) has the expected value for six magnetically independent radicals ( $2.21 \text{ cm}^3 \text{ K mol}^{-1}$ ). Upon cooling,  $\chi T$  is almost constant down to 100 K, and then



**Figure 6.** Molecular structure of 1 by X-ray diffraction on a single crystal. The hydrogen atoms and the disorder of the imino-nitroxide moiety have been removed for clarity.

decreases continuously down to 2 K (Figure 7). The data were well fitted with a Curie–Weiss law considering six spins of  $S = 1/2$  and a Weiss constant  $\theta = -1.86$  K. This behavior is in agreement with six radical moieties in the compound and very small and almost nonsignificant antiferromagnetic interactions between.

## CONCLUSION

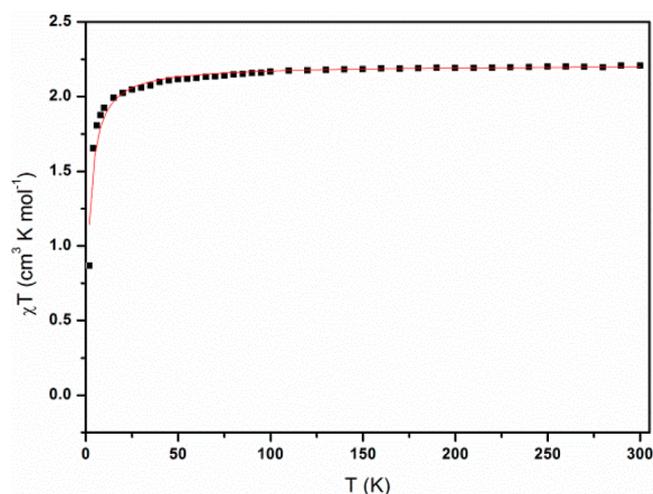
A homogeneous neutral hexaradical architecture consisting of six imino nitroxide radical moieties covalently bonded on a cyclotriphosphazene scaffold was synthesized. This is the first report for hexasubstituted cyclotriphosphazene bearing Ullman radicals appended on each arm. 1 was characterized unambiguously by EPR, MALDI-TOF, and X-ray. Straightforward methods based on various techniques were established to characterize and to quantify the number of radicals. UV–vis

Table 3. Selected Bond Lengths (Å) of Hexaradical 1

Cyclotriphosphazene Moiety			
P1–O1	1.573(3)	P1–N1	1.573(4)
P1–O4	1.578(3)	P1–N3	1.575(4)
P2–O2	1.567(4)	P2–N2	1.555(5)
P2–O5	1.568(4)	P2–N1	1.577(4)
P3–O6	1.575(4)	P3–N3	1.571(4)
P3–O3	1.581(4)	P3–N2	1.585(5)
Cyclotriphosphazene Imino Nitroxide Bridge			
C1–O1	1.401(6)	C40–O4	1.393(5)
C14–O2	1.400(7)	C53–O5	1.376(7)
C27–O3	1.396(7)	C66–O6	1.402(7)
Imino Nitroxide Moiety			
N4–O7	1.318(11)	N10–O10A	1.298(2)
N6–O8A	1.299(2)	N11–O10B	1.298(2)
N7–O8B	1.300(2)	N12–O11	1.299(2)
N9–O9	1.297(2)	N15–O12A	1.299(2)

Table 4. Selected Bond Angles (deg) of Hexaradical 1

Cyclotriphosphazene Moiety			
P1–N1–P2	121.5(3)	N1–P1–N3	117.4(2)
P2–N2–P3	122.7(3)	N2–P2–N1	116.8(2)
P3–N3–P1	120.9(2)	N3–P3–N2	117.7(2)
Cyclotriphosphazene Imino Nitroxide Bridge			
O1–P1–O4	99.43(18)	O6–P3–O3	99.7(2)
O2–P2–O5	94.9(2)	N1–P1–O4	112.9(2)
O1–P1–N1	109.6(2)	N3–P1–O4	105.4(2)
O1–P1–N3	110.55(19)	O5–P2–N1	109.5(2)
O2–P2–N1	111.5(3)	N2–P2–O5	112.7(3)
N2–P2–O2	109.3(2)	N3–P3–O6	112.6(2)
N3–P3–O3	108.8(2)	O6–P3–N2	105.1(2)
O3–P3–N2	111.4(3)	C27–O3–P3	123.9(3)
C1–O1–P1	123.8(3)	C40–O4–P1	128.2(3)
C14–O2–P2	122.4(3)	C53–O5–P2	122.1(3)
		C66–O6–P3	122.6(3)
Imino Nitroxide Moiety			
N5–C7–N4	108.4(7)	N10–C46–N11	111.7(6)
N7–C20–N6	108.7(7)	N13–C59–N12	110.2(7)
N9–C33–N8	105.0(7)	N14–C72–N15	107.9(9)

Figure 7. Temperature dependence of the product of the magnetic susceptibility with temperature ( $\chi T$ ) for 1·0.5 toluene.

spectroscopy and SWV analyses both demonstrated the presence of six radicals on the target compound. Thanks to their easy accessibility in most laboratories, these techniques were demonstrated to be chosen tools for quantitative analyses of other multiradical compounds. SQUID also confirmed the presence of imino nitroxide radicals. Electrochemical characterization by CV revealed that the oxidation process of **1** is quasi-reversible and the reduction process is reversible. As the cyclotriphosphazene ring has no significant effects on the redox potentials of radical moieties, such compounds could be interesting platforms to obtain  $-P=N-$  backbone radical polymers.

## EXPERIMENTAL SECTION

**General.** All reagents, purchased from fine chemical suppliers Aldrich, Merck, Alfa Aesar, and Fluka, were used without further purification unless otherwise stated. Hexachlorocyclotriphosphazene was purified by sublimation. Solvents were visualized either as commercially supplied or used as purified by standard techniques. Anhydrous THF was freshly distilled over sodium/benzophenone media.

**Methods.** Nonaqueous reactions were performed in oven-dried glassware under argon atmosphere at reported temperature. Reactions were monitored by thin layer chromatography on Merck silica gel 60 F254 precoated aluminum sheets. Spots were visualized either by UV 254 nm light or by staining with acidic ninhydrin solution. Column chromatography was performed on Merck silica gel 60 (230–400 mesh size) using the appropriate solvent system as eluent.

**Melting Points.** Melting points were obtained using Stuart SMP3 melting point apparatus and were uncorrected.

**Elemental Analysis.** Elemental analysis was performed on a Thermo Finnigan Flash 1112 Series Elemental Analyzer operated at The Scientific and Technological Research Council of Turkey (TUBITAK), Marmara Research Center, Institute of Chemical Technology.

**Infrared Spectroscopy.** Infrared spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring diamond/ZnSe plate. Samples were deposited as neat on ATR module, and absorption maxima ( $\nu_{\max}$ ) were quoted in wavenumbers ( $\text{cm}^{-1}$ ) in the range of 4000–650  $\text{cm}^{-1}$ . Intensities of absorptions are abbreviated as s, strong; m, medium; and w, weak.

**NMR Spectroscopy.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  nuclear magnetic resonance spectra were taken on either a Varian Unity INOVA 500 MHz or a Bruker Ultrashield Plus 400 MHz FT-NMR spectrometer. Deuterated solvents were used in all NMR measurements. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to residual solvent peaks as an internal reference for  $^1\text{H}$ – $^{13}\text{C}$  nuclei or relative to 85%  $\text{H}_3\text{PO}_4$  as an external reference for  $^{31}\text{P}$  nucleus. Assignments were determined on the basis of either unambiguous chemical shift or coupling patterns. Peak multiplicities are defined as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, and coupling constants ( $J$ ) are reported in hertz.

**Mass Spectra.** Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Microflex LT spectrometer using reported matrixes.

**Absorption Spectroscopy.** Absorption spectra were recorded at room temperature on a Shimadzu UV-2600 UV–vis spectrometer using a 1 cm path length quartz cuvette between 200 and 900 nm. Solutions were prepared in spectro-grade solvents. Molar extinction coefficients ( $\epsilon$ ) were determined by measurement of the absorption of at least six solutions of differing concentration for each radical, followed by determination of the slope.

**Electrochemical Analyses.** Electrochemical measurements were carried out on a CH Instruments 842B model workstation. The setup was a conventional three-electrode cell equipped with a glassy carbon working electrode, platinum wire counter electrode, and  $\text{Ag}/\text{AgNO}_3$  reference electrode. The glassy carbon electrode was polished routinely with 0.05  $\mu\text{m}$  alumina powder/water slurry on pads before

running experiments. All measurements of samples were recorded as reported analyte concentration in 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> electrolyte solutions of acetonitrile. Solutions were deaerated with argon purge for 5 min and kept under a blanket of argon during the experiments. All electrochemical measurements were performed at ambient temperature. Ferrocene was used as internal reference, and all potentials were referenced to a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple ( $E_{1/2}$ : 0.416 V vs SCE<sup>25</sup>). All potentials as  $E_{1/2} = (E_{pa} + E_{pc})/2$  were reported versus saturated calomel electrode (SCE). Scan rate was 50 mV/s for all cyclic voltammetry (CV) experiments. Parameters for all square-wave voltammetry (SWV) experiments are amplitude 20 mV, frequency 8 Hz, and step increment 4 mV.

The 3 mm-diameter glassy carbon working electrode (CHI104), nonaqueous Ag/Ag<sup>+</sup> reference electrode with porous Teflon tip (CHI112), platinum wire counter electrode (CHI115), and electrode polishing kit (CHI120) were purchased from CH Instruments. Supporting electrolyte, *n*-Bu<sub>4</sub>NBF<sub>4</sub>, was purchased from Alfa Aesar and dried overnight at 70 °C under vacuum. Ferrocene was supplied by Fluka, AgNO<sub>3</sub> by Carlo Erba, and anhydrous acetonitrile by VWR.

**Electron Paramagnetic Resonance (EPR) Spectroscopy.** The EPR solution spectra were recorded with a Jeol JES FA 300 X-band (9.6 GHz) spectrometer, with 100 kHz magnetic field modulation. Modulation amplitude was kept below the estimated peak-to-peak width for all spectra. Spectra were simulated using the Jeol IsoSimu computer program to obtain the value of *g*, isotropic hyperfine coupling constants (*a<sub>N</sub>*), and line width ( $\Delta H_{p-p}$ ). Typical concentration of the radicals is 10<sup>-4</sup> M in the dichloromethane–toluene (1:1) mixture. Solutions in spectro-grade solvent mixture were degassed by bubbling argon through the solutions for 30 min. Spectra for degassed solutions of the radicals were recorded at the reported temperature.

**X-ray Diffraction Analysis.** The X-ray diffraction data of the polyradical **1** were collected with a Bruker APEX II QUAZAR three-circle diffractometer using monochromatized Mo K<sub>α</sub> X-radiation ( $\lambda = 0.71073$  Å) using  $\varphi$  and  $\omega$  technique. The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS).<sup>26</sup> Space groups were determined using XPREP implemented in APEX2.<sup>27</sup> Final refinement and cif file were driven with SHELXTL package.<sup>28</sup>

**Magnetic Measurements.** Magnetic susceptibility data were collected on a polycrystalline sample on a Quantum Design MPMS-XL SQUID magnetometer under an applied magnetic field of 0.1 T and temperature range 2–300 K. All data were corrected for the contribution of the sample holder, and the diamagnetism of the samples was estimated from Pascal's constants.<sup>29</sup>

**Syntheses.** 2,3-Dimethyl-2,3-dinitrobutane (**11**), compound **4**, and compound **3** were synthesized according to published methods of refs **30**, **16**, and **10**, respectively. Reference radical **7** and target hexaradical **1** were synthesized with some modifications based on Ullman<sup>14</sup> and Shimono<sup>15</sup> protocols. Synthetic procedures of **11**, **4**, and **7** are provided in the Supporting Information.

**Hexa-(4-formylphenoxy)cyclotriphosphazene (3).** Hexachlorocyclotriphosphazene (**5**) (3 mmol, 1.044 g), 4-hydroxybenzaldehyde (**6**) (19.8 mmol, 2.416 g), and K<sub>2</sub>CO<sub>3</sub> (59.4 mmol, 8.197 g) were charged into a 100 mL flask, and then dry THF (30 mL) was added. The mixture was stirred at ambient temperature for 3 days. Reaction was filtered off, and the precipitate was washed with THF (3 × 30 mL). The filtrates and mother liquor were combined, and then concentrated to dryness to afford a beige solid. The crude product was washed with water, then with Et<sub>2</sub>O, and finally dried under vacuum to give 2.534 g of a white powder. Yield 98%. mp 160–162 °C. FT-IR (ATR,  $\nu_{\max}$  cm<sup>-1</sup>): 3103w, 3051w, 2823w, 2792w, 2733w, 1702s, 1596s, 1584s, 1500s, 1424m, 1389m, 1301m, 1267m, 1205s, 1177s, 1153s, 1104m, 1011m, 959s, 885s, 826s, 745s, 718s, 704s. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.93 (s, 6H, –CHO), 7.73 (d, 12H, *J* = 8.6 Hz), 7.14 (d, 12H, *J* = 8.6 Hz) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  190.37, 154.49, 133.74, 131.36, 121.17 ppm. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  7.09 ppm. MALDI-TOF mass (2,5-dihydroxycinnamic acid, *m/z*): C<sub>42</sub>H<sub>30</sub>N<sub>3</sub>O<sub>12</sub>P<sub>3</sub> [calcd] 861, [found] 862 [M + H]<sup>+</sup>.

**Hexa-[4-(1-oxyl-4,4,5,5-tetramethyl-2-imidazoline-2-yl)phenoxy]cyclotriphosphazene (1).** Hexa-(4-formylphenoxy)-

cyclotriphosphazene (**3**) (1 equiv, 0.8 mmol, 0.690 g), 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**4**) (1.5 equiv, 7.2 mmol, 1.066 g), and TsOH (0.1 equiv, 0.48 mmol, 0.091 g) were charged into a Schlenk tube. MeOH (4 mL) was added and then purged with argon, and the content was stirred vigorously at room temperature under argon for 14 days. The reaction mixture was washed with H<sub>2</sub>O (2 × 20 mL) twice, and eventually collected by centrifuge. The obtained precipitate was dried in a vacuum to give a yellowish solid.

FT-IR and MALDI-TOF mass analyses of the yellowish solid (as crude product) confirmed its structure as hexa-[4-(1-hydroxy-4,4,5,5-tetramethyl-2-imidazoline-2-yl)phenoxy]cyclotriphosphazene (**2**). Crude product of **2** was subjected to NaIO<sub>4</sub> oxidation without further purification. mp 214 °C with decomposition. FT-IR (ATR,  $\nu_{\max}$  cm<sup>-1</sup>) of compound **2**: 3192w, 2977w, 2925w, 2866w, 1602m, 1537s, 1500s, 1456m, 1409m, 1394m, 1378m, 1341m, 1269m, 1202s, 1158s, 1120m, 1104m, 1050w, 1034w, 1011m, 943s, 884s, 849s, 746m, 680m. MALDI-TOF mass of compound **2** (sinapinic acid, *m/z*): C<sub>78</sub>H<sub>102</sub>N<sub>15</sub>O<sub>12</sub>P<sub>3</sub> [calcd] 1534, [found] 1540 [M + 6H]<sup>+</sup>.

Yellowish solid **2** was suspended in CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and placed in an ice-bath. PO<sub>4</sub>-buffer solution (aqueous, pH 7, 120 mL) was added to the suspension and stirred vigorously. NaIO<sub>4</sub> (2 equiv, 9.6 mmol, 2.054 g) in H<sub>2</sub>O (30 mL) was added to the mixture. The color turned orange after 5 min. It was stirred for 2 h in an ice-bath. Phases were separated. The orange organic phase was washed with H<sub>2</sub>O (3 × 150 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated to dryness. Orange oily product was purified with column chromatography on silica gel eluting with a diethyl ether–dichloromethane–methanol mixture of 80–40–4 solvent ratio. Column purification gave 0.514 g of a crimson oil of **1** in 42% yield (from aldehyde). Crystallization of crimson oil in ethyl acetate–toluene–heptane mixture for 11 days in the dark at room temperature afforded crimson crystals suitable for X-ray diffraction. mp 204–206 °C. FT-IR (ATR,  $\nu_{\max}$  cm<sup>-1</sup>): 3077w, 2979w, 2929w, 2862w, 1737w, 1606m, 1496s, 1460m, 1447m, 1407m, 1388w, 1375m, 1367m, 1306m, 1292w, 1265s, 1201s, 1183s, 1161s, 1100m, 1018m, 944s, 884s, 850s, 810w, 783m, 748s, 725m, 687w, 660m. MALDI-TOF mass (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene]-malononitrile, *m/z*) [M]: C<sub>78</sub>H<sub>96</sub>N<sub>15</sub>O<sub>12</sub>P<sub>3</sub> [calcd], 1528, [found] 1529 [M + 1]<sup>+</sup>. Anal. Calcd for C<sub>78</sub>H<sub>96</sub>N<sub>15</sub>O<sub>12</sub>P<sub>3</sub>: C, 61.29; H, 6.33; N, 13.74. Found: C, 61.62; H, 6.42; N, 13.59.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01976.

Detailed experimental procedures and figures (PDF)  
CIF data report (PDF)

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### Notes

The authors declare no competing financial interest.

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