



(This article was presented to the 28th National Chemistry Congress and submitted to JOTCSA as a full manuscript)

## Nitroaromatic Compound Sensing Application of Hexa-Armed Dansyl End-Capped Poly( $\epsilon$ -Caprolactone) Star Polymer With Phosphazene Core

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**Abstract:** Hexa-armed dansyl end-capped poly( $\epsilon$ -caprolactone) star polymer with phosphazene core (**N<sub>3</sub>P<sub>3</sub>-(PCL-Dansyl)<sub>6</sub>**) was prepared in a two-step synthetic procedure including ring opening polymerization (ROP) of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) and esterification reactions. The obtained fluorescence-active polymer was employed as a fluorescent probe towards certain nitroaromatic compounds (2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2-nitrotoluene, 3-nitrotoluene, 2,4,6-trinitrophenol (picric acid), 2,4-dinitrophenol, 4-nitrophenol, and 1,2-dinitrobenzene). Fluorescence intensity of **N<sub>3</sub>P<sub>3</sub>-(PCL-Dansyl)<sub>6</sub>** was decreased gradually upon the addition of nitroaromatic compounds and the highest quenching efficiency was found to be 100% with TNT. Besides, **N<sub>3</sub>P<sub>3</sub>-(PCL-Dansyl)<sub>6</sub>** gave exceptionally selective response toward nitroaromatic compounds, even in the presence of toxic metal cations such as Pb<sup>2+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>.

**Keywords:** Nitroaromatic compounds; dansyl-functional star polymer; fluorescence spectroscopy.

**Submitted:** July 22, 2016. **Accepted:** August 26, 2016.

**Cite this:** Dandan Dođancı M, Bayır S, Dođancı E, Görür M, Yılmaz F. Nitroaromatic Compound Sensing Application of Hexa-Armed Dansyl End-Capped Poly( $\epsilon$ -Caprolactone) Star Polymer With Phosphazene Core. JOTCSA. 2016;3(3):501–14.

**DOI:** 10.18596/jotcsa.36573.

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## INTRODUCTION

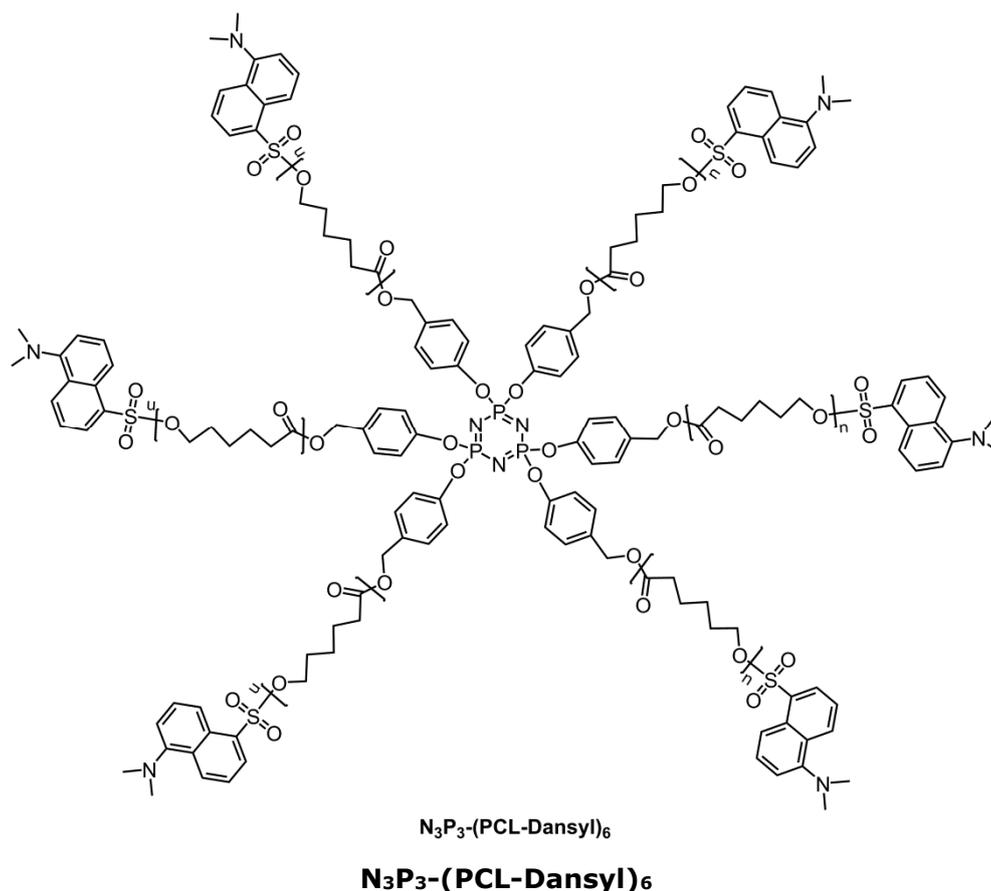
Nitroaromatics are organic molecules which contain one or more nitro groups ( $\text{NO}_2$ ) attached to the aromatic ring. These compounds are registered as environmentally hazardous materials by U.S. Environmental Protection Agency [1, 2]. Among them, 2,4,6-trinitrotoluene (TNT) and nitrophenols, such as 4-nitrophenol (4-NP), and picric acid (2,4,6-trinitrophenol, PA), are important pollution sources. TNT is best known as an explosive material for military and terrorist activities, industrial, and mining applications [3-5]. When it enters the environment, a small amount of it is enough to cause health problems such as headaches, anemia, and skin irritation. Picric acid is another explosive material which is even stronger than TNT. Since it is highly soluble in water, it can easily contaminate water and environment [6]. Meanwhile, 4-NP is one of the highly hazardous and toxic phenols which are used in the production of various analgesics, pesticides, dyes and processing of leather [2]. Besides their toxicities to humans, animals, and plants, and they give an undesirable taste and odor to drinking water, even in very low concentration [7-9]. Decontamination of wastewaters from these pollutants is very difficult since they are usually resistant to microbial degradation [9, 10]. Therefore, accurate, rapid and selective detection of nitroaromatics is very crucial in many areas, such as environmental science, public security, and forensics.

Different methods have been reported for detection of trace amounts of nitroaromatic compounds [9-13]. Among them, fluorescence spectroscopic method has many advantages related to sensitivity, selectivity, and response time [11-14]. Therefore, fluorescence chemosensors were used for the detection of various analytes such as cations, anions, nitroaromatics, biological entities, *etc.* [15-18]. Dansyl-based polymers have been employed as fluorescent probes due to strong fluorescence and relatively long emission wavelength of dansyl unit in the visible region as well as its structural flexibility for derivatization [18-21]. Gorur *et al.* synthesized hexa-armed dansyl end-functional poly( $\epsilon$ -caprolactone) (PCL) star polymer with phosphazene core for the selective fluorescence detection of  $\text{Pb}^{2+}$  cation [18]. Murariu *et al.* prepared optically active dansyl-labeled copolyacrylates for sensitive and selective detection of transition metal ions. They showed that the dansyl side-functional copolymers selectively responded the presence of  $\text{Fe}^{2+}$  cations [22]. Dansyl-containing polymers were mainly used for the fluorescent detection of ionic species. They were rarely used as fluorescence probes against nitroaromatic compounds. Buruiana *et al.* synthesized two acrylic copolymers containing dansyl groups by free radical polymerization to be used in fluorescence detection of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  metal ions as well as some of nitroaromatic compounds (picric acid, p-nitrotoluene, nitrobenzene, *etc.*) in organic medium. They concluded that the fluorescence

emission of the polymer films were quenched by nitrobenzene vapors and the nitroaromatic compounds had a higher degree of fluorescence quenching [23]. To the best of our knowledge, there is no other report in the literature that uses dansyl-based fluorescent polymers for detection of nitroaromatic compounds.

Star-shaped polymers consist of several linear chains connected to a central core and have many advantages due to their compact molecular shapes, highly branched structures and unique rheological properties [24-34]. They are highly soluble in organic solvents, have smaller hydrodynamic volume and radius of gyration, resulting in their lower solution and melt viscosities with respect to linear polymers with similar molecular weights [32]. Besides, star polymers demonstrate less chain entanglements than the linear ones [27, 32]. There are two main approaches to synthesize star polymers: divergent (core-first) and convergent (arm-first). In the divergent method, the polymerization starts from multifunctional initiators and the number of arms of the star polymer is determined by the number of initiating functional groups on the initiator [26, 28-32]. On the other hand, the convergent method requires the preparation of polymer arms with suitable functional groups and followed by a coupling or terminating reaction with a multifunctional core compound [26, 30, 33, 34].

In one of our previous studies, we prepared dansyl end-functional PCL star polymer with a phosphazene core ( $N_3P_3-(PCL-Dansyl)_6$ , see Scheme 1) via ring opening polymerization (ROP) of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) and esterification reactions. Then,  $N_3P_3-(PCL-Dansyl)_6$  was used as fluorescent chemical probe for the detection of transition metal cations [18]. In this report, the same star polymer was employed as fluorescent chemical sensing agent for the determination of nitroaromatic compounds. Chemical structures of the obtained polymers were confirmed by FTIR and  $^1H$ -NMR spectroscopic techniques.



**Scheme 1:** Hexa-armed dansyl end-capped poly( $\epsilon$ -caprolactone) star polymer with phosphazene core ( $\text{N}_3\text{P}_3\text{-(PCL-Dansyl)}_6$ ).

## MATERIALS AND METHODS

**Materials.** All chemicals used were of analytical grade or of the highest purity available. 2,4,6-trinitrotoluene (1 mg/mL TNT solution), 2,4-dinitrotoluene (2,4-DNT, 97%), 2,6-dinitrotoluene (2,6-DNT, 98%), 2-nitrotoluene (2-NT,  $\geq 99\%$ ), 3-nitrotoluene (3-NT, 99%), 2,4,6-trinitrophenol (picric acid, PA,  $\geq 98\%$ ), 2,4-dinitrophenol (2,4-DNP,  $\geq 98\%$ ), 4-nitrophenol (4-NP,  $\geq 99\%$ ), 1,2-dinitrobenzene (1,2-DNB,  $\geq 99\%$ ) were all purchased from Sigma-Aldrich. The molecular structures of nitroaromatic compounds used in the present study are given in Scheme 2. Tetrahydrofuran (THF) used as solvent was purchased from Sigma-Aldrich.

**Instrumentation.**  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR, FTIR spectroscopy techniques were used for characterization of the synthesized polymer.  $^1\text{H}$  and  $^{31}\text{P}$ -NMR spectra were measured on a Varian UNITY INOVA 500 MHz (202 MHz for  $^{31}\text{P}$ ) spectrometer in  $\text{CDCl}_3$  and  $\text{d}_6\text{-DMSO}$  solutions at 25 °C. ATR-FTIR spectra were obtained on Perkin-Elmer Spectrum Two™ spectrometer equipped with Perkin Elmer UATR Two diamond ATR accessory and the results were uncorrected. The molecular weight of the polymers was characterized by

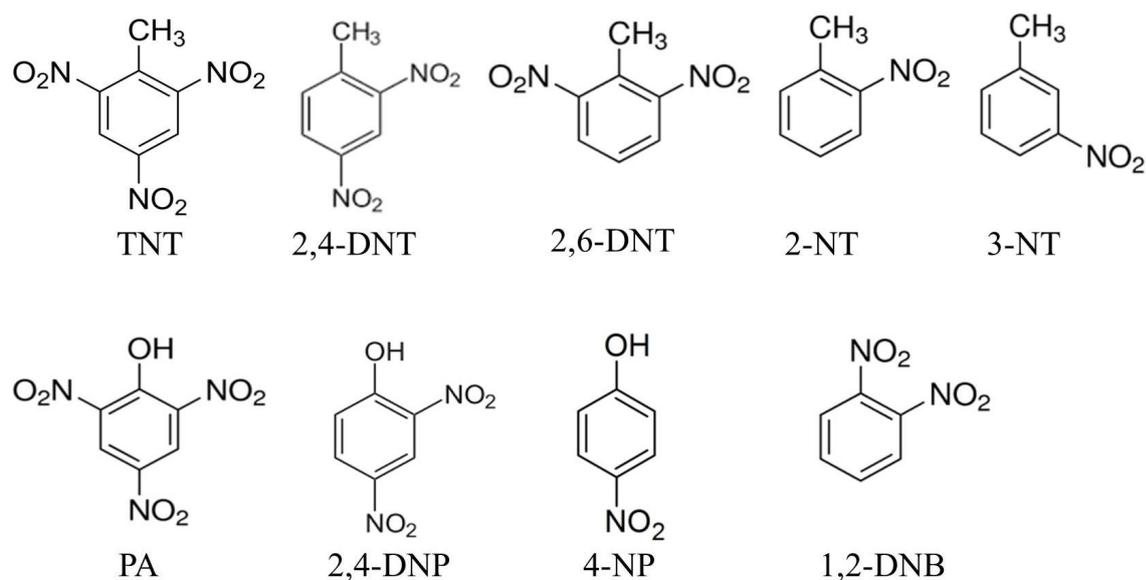
Agilent 1260 Infinity GPC/SEC Instruments. Thermal properties of the obtained polymers were analyzed by Perkin Elmer DSC 8500 double-furnace differential scanning calorimeter and Perkin Elmer STA 6000 simultaneous thermal analyzer, respectively. UV-Vis and fluorescence spectra were measured using quartz cuvettes (1 cm path length) on Shimadzu UV-2600 and Agilent Cary Eclipse spectrophotometers, respectively.

**Synthesis of dansyl end-capped poly( $\epsilon$ -caprolactone) star polymer with phosphazene core ( $N_3P_3$ -(PCL-Dansyl) $_6$ ).**  $N_3P_3$ -(PCL-Dansyl) $_6$  was prepared according to the method reported in the literature [18]. Details are given in Supporting Information.

**Nitroaromatic sensing applications of dansyl end-capped PCL star polymer via fluorescence spectroscopy.** Nitroaromatic sensing applications of  $N_3P_3$ -(PCL-Dansyl) $_6$  were performed via fluorescence spectroscopy. Fluorescence emission spectra were obtained with Agilent Cary Eclipse spectrophotometers with an excitation wavelength 328 nm in THF solutions. Firstly, definite amounts of  $N_3P_3$ -(PCL-Dansyl) $_6$  were dissolved in THF at room temperature. Then, the fluorescent responses of star PCL polymer upon the addition of prescribed amount of targeted nitroaromatics were measured.

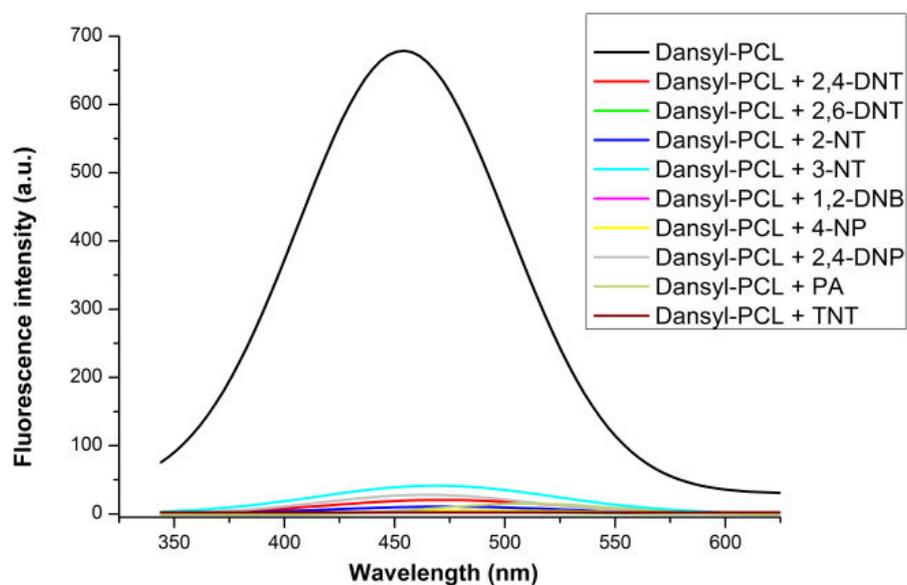
## RESULTS AND DISCUSSION

The dansyl end-capped PCL star polymer with phosphazene core ( $N_3P_3$ -(PCL-Dansyl) $_6$ ) was successfully synthesized in a two-step synthetic procedure reported in the literature (see Supporting Information for the detailed description) [18]. The dansyl fluorophore had strong fluorescence emission in the visible region with high quantum yields [18, 35]. It consists of two main parts in its molecular structure. Dimethylamino moiety works as the electron donor while sulfonic acid group acts as the acceptor. Because of these characteristics, dansyl fluorophore was widely used as fluorescent probe for the detection of various materials [18-22] or as a label for bio-imaging [36, 37].

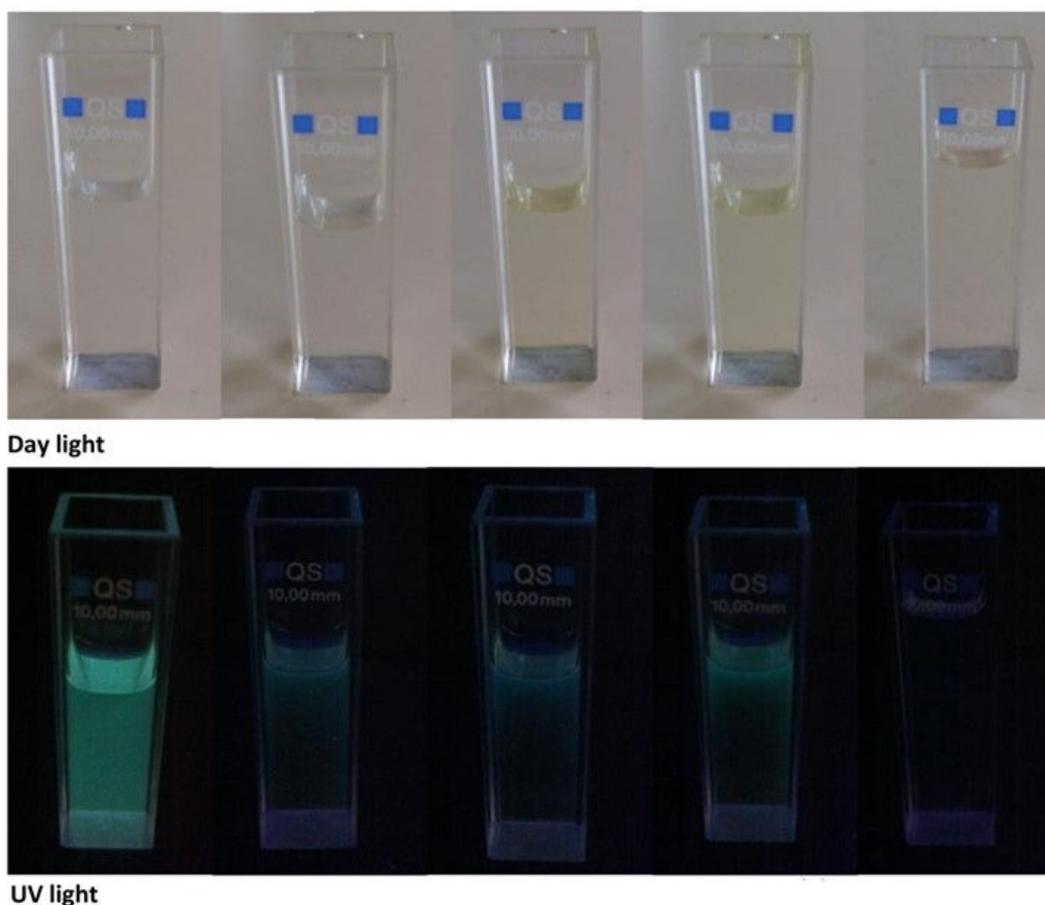


**Scheme 2.** The molecular structures of nitroaromatic compounds used in the present study.

The binding behavior and recognition characteristics of the dansyl end-capped PCL star polymer toward several nitroaromatic compounds were determined via fluorescence spectrophotometric measurements using 1-cm path length cuvettes. The solutions were prepared fresh in THF solution and the analysis performed at 328 nm excitation wavelengths at room temperature. The fluorescence emission spectra of dansyl end-capped PCL star polymer with phosphazene core upon addition of 50 equivalent of nitroaromatic compounds are given in Figure 1. It can be seen from the figure that all nitroaromatic compounds in this study quenched fluorescence emission of dansyl fluorophore efficiently. The highest quenching efficiency was observed for TNT and 4-NP. The photographs of the  $1.27 \times 10^{-5}$  M bare **N<sub>3</sub>P<sub>3</sub>-(PCL-Dansyl)<sub>6</sub>** solutions and with 50 equivalent of 4-NP, 2,4-DNP, PA, and TNT under daylight and UV-light ( $\lambda_{\text{ext}}=365$  nm) were given in Figure 2. As seen in the figure, upon the addition of 50 equivalent of TNT, fluorescence emission of the dansyl unit were quenched completely.

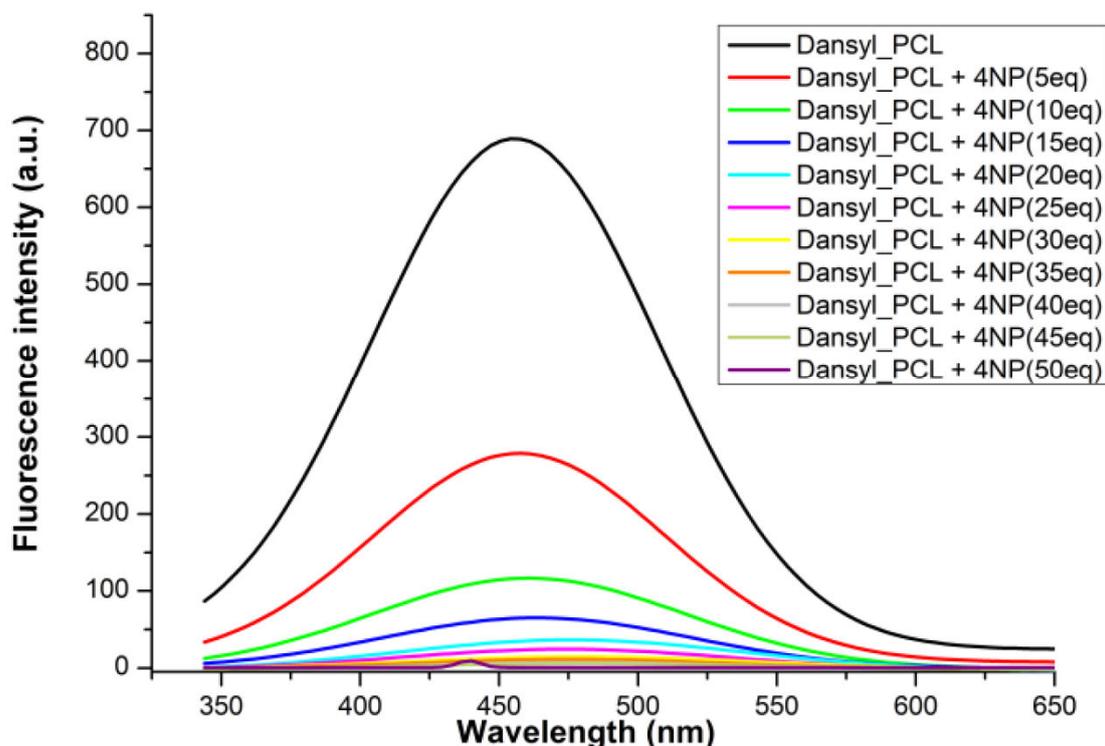


**Figure 1.** The fluorescent emission spectra ( $\lambda_{\text{ex}} = 328 \text{ nm}$ ) of  $\text{N}_3\text{P}_3\text{-(PCL-Dansyl)}_6$  ( $1.27 \times 10^{-5} \text{ M}$ ) in THF upon addition of 50 eq. of different nitroaromatic compounds.



**Figure 2.** Photograph of  $\text{N}_3\text{P}_3\text{-(PCL-Dansyl)}_6$  ( $1.27 \times 10^{-5} \text{ M}$ ) with 50 eq of 4-NP, 2,4-DNP, PA, and TNT (from left to right) under day light and UV light ( $\lambda_{\text{ext}} = 365 \text{ nm}$ ).

The evolution of fluorescence emission spectra of dansyl end-capped PCL upon titration with 4-NP at different equivalent ratios are given in Figure 3. The fluorescence intensity was found to decrease significantly as a function of concentration.

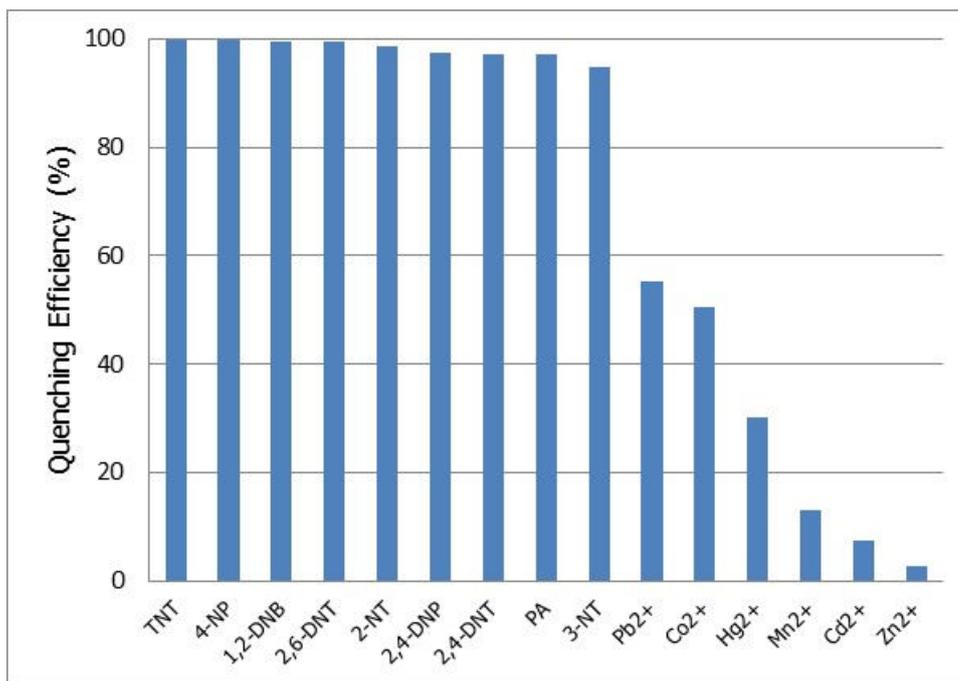


**Figure 3.** Fluorescence emission spectra of  $N_3P_3-(PCL-Dansyl)_6$  ( $1.27 \times 10^{-5}$  M) in THF in the presence of 4-NP at 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 equivalent ratios.

Quenching efficiency ratios (QE) were calculated using equation 1:

$$QE = \left( \frac{I_0 - I}{I_0} \right) \times 100 \quad (\text{Eq. 1})$$

where,  $I_0$  is the fluorescence intensity without nitroaromatic compounds and  $I$  is the fluorescence intensity observed in the presence of the nitroaromatic compounds. The highest quenching efficiency was obtained for TNT as 100% and for 4-NP as 99.37%. It can be said that nitrophenols had high quenching values. The sensing performance was found to be selective toward nitroaromatic compounds, even in the presence of toxic metal cations such as  $Pb^{2+}$ ,  $Co^{2+}$ ,  $Hg^{2+}$ ,  $Mn^{2+}$ ,  $Cd^{2+}$  and  $Zn^{2+}$  as seen from Figure 4.



**Figure 4.** Quenching efficiency ratios for fluorescent emission intensities of **N<sub>3</sub>P<sub>3</sub>-(PCL-Dansyl)<sub>6</sub>** upon addition of 50 eq. nitroaromatic compounds and metal cations.

## CONCLUSION

The dansyl end-capped poly( $\epsilon$ -caprolactone) star polymer with phosphazene core (**N<sub>3</sub>P<sub>3</sub>-(PCL-Dansyl)<sub>6</sub>**) could serve as an alternative nitroaromatic compound sensor due to the strong sensitivity, selectivity, and synthetic simplicity. The fluorescent intensity of **N<sub>3</sub>P<sub>3</sub>-(PCL-Dansyl)<sub>6</sub>** was decreased gradually upon the addition of nitroaromatic compounds and the highest quenching efficiency was found to be 100% with TNT. The sensing performance was found to be selective toward nitroaromatic compounds, even in the presence of toxic metal cations such as Pb<sup>2+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>.

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**Türkçe Öz ve Anahtar Kelimeler****Fosfazen Çekirdeđi İçeren Altı Kollu Dansil Uçlu Poli( $\epsilon$ -Kapolakton) Yıldız Polimerinin Nitroaromatik Bileşikleri Hissetme Uygulaması**

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**Öz:** Altı kollu, dansil uçlu ve fosfazen çekirdekli poli( $\epsilon$ -kapolakton) yıldız polimeri (**N<sub>3</sub>P<sub>3</sub>-(PCL-Dansil)<sub>6</sub>**) iki adımlı sentez prosedürü ile hazırlanmıştır. Yürütölen adımlar  $\epsilon$ -kapolaktonun ( $\epsilon$ -CL) halka açılması ve esterleştirme tepkimeleri içermektedir. Elde edilen floresans aktif polimer belli nitroaromatik bileşiklerin (2,4,6-trinitrotoluen, TNT; 2,4-dinitrotoluen; 2,6-dinitrotoluen; 2-nitrotoluen; 3-nitrotoluen; 2,4,6-trinitrofenol, pikrik asit; 2,4-dinitrofenol; 4xnitrofenol ve 1,2-dinitrobenzen) hissedilmesi için floresan prob olarak kullanılmıştır. **N<sub>3</sub>P<sub>3</sub>-(PCL-Dansil)<sub>6</sub>** polimerinin floresans şiddeti nitroaromatik bileşiklerin ilavesiyle yavaş yavaş azalmaktadır ve en yüksek söndürme etkinliđi TNT ile %100 oranında sağlanmıştır. Bunun yanında, **N<sub>3</sub>P<sub>3</sub>-(PCL-Dansil)** nitroaromatik bileşiklere karşı çok seçici tepki vermektedir, hatta ortamda Pb<sup>2+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> ve Zn<sup>2+</sup> gibi zehirli metal katyonları varlığında bile seçimliliđini kaybetmemektedir.

**Anahtar kelimeler:** Nitroaromatik bileşikler; dansil fonksiyonlu yıldız polimer; floresans spektroskopisi.

**Gönderilme:** 22 Temmuz 2016. **Kabul:** 26 Ağustos 2016.

